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(54) HIGH MANGANESE POLYCRYSTALLINE ANODE MATERIAL, PREPARATION METHOD THEREOF AND DYNAMIC LITHIUM ION BATTERY

(57) A high manganese polycrystalline anode material has a formula: $Li_wMn_x(CoNi)_yO_z$, wherein x=0.4~2.0, y=0.1 ~0.6, x+y<2, z≥2, W≥1, wherein weight of Mn is at least 40% weight of $Li_wMn_x(CoNi)_yO_z$, particle size thereof is 7~20μm, wherein the high manganese polycrystalline anode material is consisted of at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n (NiMn)_{1-n}O_2$, $LiNi_{0.8} Co_{0.2}O_2$, $LiCoO_2$, $LiNiMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)}O_4$ and $LiNiO_2$, wherein n<1, and the crystalline textures are in a symbiotic and mixed phase. The specific energy of the anode material is more than 155Wh/K, the capacity retention is not less than 80% after 500 charging and discharging circles when the charging and discharging rate is 1C at 55 °C, the circulation life span at 25 °C is not less than 1000times, the capacity is maintained above 80%, and the processability of the anode material is good.

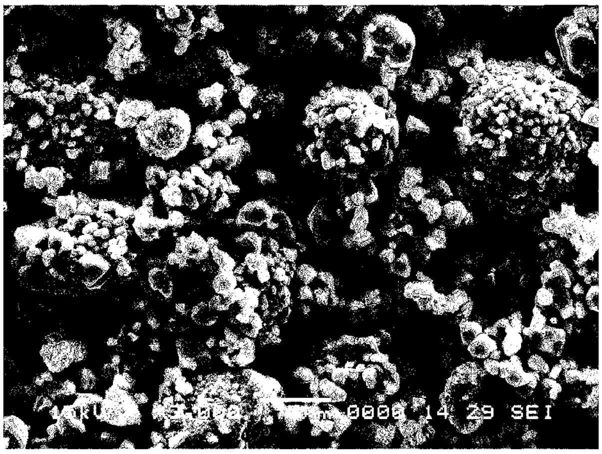

FIG.14

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Description

Background of the Present Invention

Field of Invention

[0001] The present invention relates to an anode material, preparing method thereof, and a lithium ion power battery, and more particularly to a high manganese polycrystalline anode material, preparing method thereof, and a lithium ion power battery prepared from the high manganese polycrystalline anode material.

Description of Related Arts

[0002] Recently, the lithium ion power battery technology has developed very fast. Accordingly, the performance, cost and security of the power battery play a significant role in the advancement of the electric automobile technology. In addition, power battery is indispensable for wind power, nuclear power, solar power, peak load regulation and new energy automobile, so that a breakthrough thereof will bring a new spring to the whole new energy industry chain, and the power battery will then be an energy storing tool for all kinds of new energy source and take place of fuel to become a main supply facility of mobile energy. Electric bicycle, as a novel energy-save and convenient transportation tool, has gradually been accepted by consumers, a number of the consumed population of the electric bicycles has amounted to 200, 000, 000 in 2007 in China, and we are glad to see that the electric automobile industry in China is gaining momentum. But a lot of problems still remain to be solved, for example, two most concerned issues are the security and environment pollution. Currently, the most widely used power battery in an electric automobile is still lead-acid battery in China domestic market, but disadvantages such as a relatively low energy density and high pollution have gradually been acknowledged. Therefore, to find a novel replaceable product has become a hot topic in the power battery field and even a challenge for the whole world. The Ni-H battery technology has been developed relatively mature, the cost is relatively low and the battery does not pollute the environment. But a fetal disadvantage, which is the memory effect, has brought a lot of inconvenience for the use of the Ni-H battery. In addition, existence of other disadvantages such as a high self-discharge rate and a low specific energy makes the Ni-H battery only be a transitional product. The lithium ion battery has gradually taken place of Ni-H battery in energy storing facilities because of its high energy density and other following advantages: 1) a high working voltage of the lithium ion battery, which is above 3.6V, is three times larger than the Cd-Ni and Ni-H battery; 2) a small size, which is 30% smaller than the Ni-H battery; 3) a low weight, which is 50% smaller than the Ni-H battery; 4) a high specific energy, which is 120~ 150wh/kg, is 2~3 times larger than the Cd-Ni battery and 1~2 times larger than the Ni-H battery; and 5) no memory effect.

[0003] Lithium colbalt oxide, which is the earliest mature anode material in industry, has advantages such as a high energy density and a good circle performance. But its application in power battery is still limited because of high cost and worrying security performance. Co-Ni-Mn ternary anode material also has advantages such as a high energy density and a good circle performance. But its application in power battery is also limited by the bottle neck of high cost and worrying security performance. Currently, the study of anode material of power battery has been focused mainly on lithium iron phosphate and lithium manganate. Lithium manganate enjoys benefits of low cost and good security performance, but a circle performance at a relatively high temperature is bad, and a high self-discharge rate is also a critical drawback. Although the performance can be modified by doping with Co, Ni, Mg and Al, it still cannot be used alone in power battery in view of the cost. Lithium iron phosphate is safe as an anode material, but an atmosphere of a preparing procedure thereof is hard to control, resulting in a low uniform rate and low energy density of the product, and the cost fact also calls a further development of the lithium iron phosphate technology if it is going to be widely used in power battery. Therefore, development of an anode material which has a relatively low cost, high security and a long life span really makes senses to the development of the power battery and electric automobile in the future.

Summary of the Present Invention

[0004] The main object of the present invention is to provide a high manganese polycrystalline anode material, preparing method thereof, and a lithium ion power battery prepared from the high manganese polycrystalline anode material, wherein the power battery has a high energy density and good circle performance at a high temperature.

[0005] Additional advantages and features of the invention will become apparent from the description which follows, and may be realized by means of the instrumentalities and combinations particular point out in the appended claims.

[0006] According to the present invention, the foregoing and other objects and advantages are attained by a high manganese polycrystalline anode material of the formula: $Li_wMn_x(CoNi)_yO_z$, wherein x=0.4~2.0, y=0.1~0.6, $x+y<2$, $z\geq2$, $W\geq1$, wherein weight of Mn is at least 40% weight of $Li_wMn_x(CoNi)_yO_z$, particle size thereof is 7~ 20μm, wherein the high manganese polycrystalline anode material is consisted of at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n (NiMn)_{1-n}O_2$, $LiNi_{0.8} Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)}O_4$ and $LiNiO_2$, wherein n<1, and the crystalline textures are in a symbiotic or mixed phase.

[0007] A mole percentage of Mn is 60~90% of Co, Ni plus Mn

[0008] A doping element in lattice of the crystalline textures is selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr, wherein a doping amount is 0.01 ~0.1 mol/mol $Li_wMn_x(CoNi)_yO_z$.

[0009] In accordance with another aspect of the invention, the present invention provides a method of preparing a high manganese polycrystalline anode material, comprising the following steps.

[0010] 1) preparing of a precursor: disperse of 0.3 ~ 1.2 mol Li_2CO_3, LiAc or LiOH in 200~300ml 2~5 wt % polyethylene glycol hydrophilic colloid solution, stir at a speed of 10~60rin/min for 50~120min to obtain a colloid product, add compound of Co, Ni and Mn thereto with a mol ratio of Mn to Ni plus Co is 0.4~2.0: 0.01~0.6, stir at a speed of 50~60rin/min for 10~30min, dry at 150~600 °C for 2~15 hours, and stir at a speed 1500~3000rin/min for 2~30min to obtain the precursor of crystalline of Li with Co, Ni and Mn

[0011] 2) sintering of a monocrystalline: sinter the precursor at 750~1000°C for 4~15 hours, cooling, and cutting a particle size thereof to D50=7~20μm so as to obtain the monocrystalline compound which is $LiMn_2O_4$, LiCon $(NiMn)_{1-n}O_2$, $LiNi_{0.8} Co_{0.2}O2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2 (1-n)} O_4$ or $LiNiO_2$, wherein n < 1.

[0012] 3) synthesizing of polycrystalline: mix at least two of the monocrystalline compounds at a mol ratio of Mn to Co plus Ni plus Mn is 60~90:100, stir at a speed of 100~150rin/min for 5~20min to obtain a mixture, wherein 0.01~0,1mol soluble salt of a doping element selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr dissolved in 100~300ml 30~60 wt % ethanol aqueous solution is added to said mixture, stir at a speed of 60~100 rin/min for 30~60min, dry at 100~200°C for 2~10 hours, heat with a heating rate of 50~100°C/hr until a temperature thereof amounts to 300~850°C, and activate for 2~10 hours, so that crystalline textures are in a symbiotic or mixed phase.

[0013] Preferably, in the method of the present invention, the crystalline textures in the symbiotic phase are subjected to a smashing process.

[0014] Preferably, in the method of the present invention, crystalline textures in a symbiotic or mixed phase are grinded at a rotating speed of 1500~3000rin/min for 2~ 5min.

[0015] The Compound of Co, Ni and Mn in the method of the present invention is selected from the group consisting of monohydroxy compound, oxalate and carbonate of the three elements.

[0016] Preferably, in the step 2), the precursor is sintered at 750~1000°C for 4~15 hours and then naturally cooled down.

[0017] In accordance with another aspect of the invention, the present invention provides a lithium ion power battery having a positive electrode, wherein current collector of the positive electrode is coated with active anode material, wherein a formula of the active anode material is $Li_wMn_x(CoNi)_yO_z$, wherein x=0.4~2.0, y=0.1~0.6, x+y<2, z≥2, W≥1, weight of Mn ≥ 40% weight of $Li_wMn_x(CoNi)_yO_z$, particle size of 7~ 20μm, wherein the high manganese polycrystalline anode material comprises at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n (NiMn)_{1-n}O_2$, $LiNi_{0.8} Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)}O_4$ and $LiNiO_2$, wherein n<1, and the crystalline textures are in a symbiotic or mixed phase.

[0018] The anode material of the battery of the present invention is prepared by the following steps: mix $Li_wMn_x (CoNi)_yO_z$, electric conductive carbon black which is 2.0~ 3.0% weight of the anode material, and binder PVDF which is 2.0~2.5% weight of the anode material to obtain a resulting mixture, add n-methyl pyrrolidone thereto with a ratio of the resulting mixture to n-methyl pyrrolidone is 1:0.9 by weight, after uniformly stirring to obtain a broth, coat the broth onto the aluminum foil current collector, dry and compress to obtain the anode material pole piece.

[0019] In comparison with the prior art, the high manganese polycrystalline anode material of the present invention has several advantages, a specific energy thereof is above 155Wh/Kg, a circulation capacity thereof is maintained above 80% after 500 circles of charge and discharge at 55 °C, a circulation life span thereof at 25 °C is not less than 1 000 times, the capacity is always above 80% and is capable of being used in a high voltage system, a charging voltage is not less than 4.3V, a good processability is provided, the anode material pole piece is not easy to slip off, and a weight of the anode material is relatively lighter which is a quarter or a fifth of a lead-acid battery under a condition that the lead-acid battery has a same amount of energy with the anode material of the present invention. Accordingly, the power battery prepared from the anode material of the present invention can be used in power system of electric bicycle, electric automobile, and energy storing system of wind power, nuclear power, solar power, peak load regulation and the like.

[0020] Still further objects and advantages will become apparent from a consideration of the ensuing description and drawings.

[0021] These and other objectives, features, and advantages of the present invention will become apparent from the following detailed description, the accompanying drawings, and the appended claims.

Brief Description of the Drawings

[0022] Fig. 1 is an x ray diffraction pattern of a sample provided by example 1 of the present invention.

[0023] Fig. 2 is a scanning electron micrograph of a sample provided by example 1 of the present invention.

[0024] Fig. 3 is an x ray diffraction pattern of a sample provided by example 2 of the present invention.

[0025] Fig. 4 is a scanning electron micrograph of a sample provided by example 2 of the present invention.

[0026] Fig. 5 is an x ray diffraction pattern of a sample provided by example 3 of the present invention.

[0027] Fig. 6 is a scanning electron micrograph of a sample provided by example 3 of the present invention.

[0028] Fig. 7 is an x ray diffraction pattern of a sample provided by example 4 of the present invention.

[0029] Fig. 8 is a scanning electron micrograph of a sample provided by example 4 of the present invention.

[0030] Fig. 9 is an x ray diffraction pattern of a sample provided by example 5 of the present invention.

[0031] Fig. 10 is a scanning electron micrograph of a sample provided by example 5 of the present invention.

[0032] Fig. 11 is an x ray diffraction pattern of a sample provided by example 6 of the present invention.

[0033] Fig. 12 is a scanning electron micrograph of a sample provided by example 6 of the present invention.

[0034] Fig. 13 is an x ray diffraction pattern of a sample provided by example 7 of the present invention.

[0035] Fig. 14 is a scanning electron micrograph of a sample provided by example 7 of the present invention.

[0036] Fig. 15 is an x ray diffraction pattern of a sample provided by example 8 of the present invention.

[0037] Fig. 16 is a scanning electron micrograph of a sample provided by example 8 of the present invention.

[0038] Fig. 17 is an x ray diffraction pattern of a sample provided by example 9 of the present invention.

[0039] Fig. 18 is a scanning electron micrograph of a sample provided by example 9 of the present invention.

[0040] Fig. 19 is an x ray diffraction pattern of an anode material of a first control example.

[0041] Fig. 20 is a scanning electron micrograph of the anode material of the above first control example.

[0042] Fig. 21 is an x ray diffraction pattern of an anode material of a second control example.

[0043] Fig. 22 is a scanning electron micrograph of the anode material of the above second control example.

Detailed Description of the Preferred Embodiment

[0044] According to a preferred embodiment of the present invention, a formula of a high manganese polycrystalline anode material is $Li_wMn_x(CoNi)_yO_z$, wherein x=0.4~2.0, y=0.1~0.6, x+y<2, z≥2, W≥1. A doping element in lattice of the crystalline textures is selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr, wherein a doping amount is 0.01~0.1 mol/mol $Li_wMn_x(CoNi)_yO_z$, wherein a weight of Mn is not less than 40% weight of $Li_wMn_x(CoNi)_yO_z$, a particle size thereof is 7~20μm. The high manganese polycrystalline anode material is consisted of at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n$ (NiMn) $_{1-n}O_2$, $LiNi_{0.8}$ $Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{(1-n)}O_4$ and $LiNiO_2$, wherein n<1, and the crystalline textures are in a symbiotic or mixed phase, a compact density thereof is 3.0~3.5 g/cm^3.

[0045] The present invention also provides a method of preparing a high manganese polycrystalline anode material, the method comprises the following steps.

[0046] 1) Preparing of a precursor: disperse of 0.3~1.2 mol Li_2CO_3, LiAc or LiOH in 200~300ml 2~5 wt % polyethylene glycol hydrophilic colloid solution, stir at a speed of 10~60rin/min for 50~120min to obtain a colloid product, add compound of Co, Ni and Mn thereto with a mol ratio of Mn to Ni plus Co is 0.4~2.0: 0.01~0.6, stir at a speed of 50~60rin/min for 10~30min, dry at 150~600°C for 2~15 hours, and stir at a speed 1500~3000rin/min for 2~30min to obtain the precursor of crystalline of Li with Co, Ni and Mn. The compound of Co, Ni and Mn in the method of the present invention is selected from the group consisting of monohydroxy compound, oxalate and carbonate of the three elements.

[0047] 2) Sintering of a monocrystalline: sintering the precursor at 750~1000°C for 4~15 hours, cooling, and cutting a particle size thereof to D50=7~20μm so as to obtain the monocrystalline compound which is $LiMn_2O_4$, LiCon (NiMn) $_{1-n}O_2$, $LiNi_{0.8}$ $Co_{0.2}O2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2\ (1-n)}$ O_4 or $LiNiO_2$, wherein n < 1.

[0048] 3) Synthesizing of polycrystalline: mix at least two of the monocrystalline compounds at a mol ratio of Mn to Co plus Ni plus Mn is 60~90:100, stir at a speed of 100~150rin/min for 5~20min to obtain a mixture, wherein 0.01~0.1mol soluble salt of a doping element selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr dissolved in 100~300ml 30~60 wt % ethanol aqueous solution is added to the mixture, stir at a speed of 60~100 rin/min for 30~60min, dry at 100~200 °C for 2~10 hours to finish the doping process, heat with a heating rate of 50~100 °C/hr until a temperature thereof amounts to 300~850°C, and activating for 2~10 hours, so that crystalline textures are in a symbiotic or mixed phase. The crystalline textures in a symbiotic or mixed phase are grinded at a rotating speed of 1500~3000rin/min for 2~ 5min to obtain the high manganese polycrystalline anode material. A formula of the high manganese polycrystalline anode material is $Li_wMn_x(CoNi)_yO_z$, wherein x=0.5~ 1.9, y=0.1~0.6, x+y<2, z≥2, W≥1, weight of Mn ≥ 40% weight of $Li_wMn_x(CoNi)_yO_z$, particle size of 7~20μm, wherein the high manganese polycrystalline anode material is consisted of at least two crystalline textures which are selected from the group consisting of $Limn_2O_4$, $LiCo_n$ (NiMn) $_{1-n}O_2$, $LiNi_{0.8}$ $Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)})O_4$ and $LiNiO_2$, wherein n<1, and the crystalline textures are in a symbiotic or mixed phase, a compact density thereof is 3.0~3.5g/cm^3.

[0049] The drying device of the present invention is a KSF1100-V oven-type furnace of Yixing Qianjing Furnace Device Co.,Ltd. The stirring device is a JJ experimental homogenizer of Langfang Shengtong Machinery Co., Ltd. The grinding device is a SHQM two-planet type grinder of Lianyuangang Chunlong Petroleum Instrument Co., Ltd. The grading equipment is a TY-200A analyzing standard grading sieve of Xinxiang Tongyi Machinery Co., Ltd. The high manganese polycrystalline anode material of the present invention is tested and analyzed with a JSM6360 scanning electron microscope of Japan Electronic Co., Ltd, a D/max-2200pc x-ray diffractometer of Japan Rigaku Co., Ltd, a LS602 laser particle size analyzer of Zhuhai Omec Co., Ltd, a FZS4-4B densitometer and a Pioneer 2002 areameter of Beijing Iron&Steel Research Institute.

[0050] The lithium ion power battery of the present invention is consisted of positive electrode, negative electrode, non-aqueous electrolytic solution, separator, and a container. The positive pole is consisted of positive current collector and active anode material coated on the positive current collector, wherein a formula of the active anode material is $Li_wMn_x(CoNi)_yO_z$, wherein x=0.5~1.9, y=0.1~0.6, x+y<2, z≥2, W≥1, a doping element in lattice of the crystalline textures is selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr, wherein a doping amount is 0.01~ 0.1mol/mol $Li_wMn_x(CoNi)_yO_z$, weight of Mn is not less than 40% weight of $Li_wMn_x(CoNi)_yO_z$, a mole percentage of Mn is 60~90% of Co, Ni plus Mn, a particle size thereof is 7~20μm, wherein the high manganese polycrystalline anode material comprises at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n(NiMn)_{1-n}O_2$, $LiNi_{0.8}Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)}O_4$ and $LiNiO_2$, wherein n<1, and the crystalline textures are in a symbiotic or mixed phase. A scanning electron micrograph suggests that the crystalline textures of the anode material is in a mixed phase, a characteristic peak of an x ray diffractrometer teaches a existence of the crystalline textures in a symbiotic phase. The compact density thereof is 3.0~3.5g/cm^3, an initial capacity of charging and discharging 1C at 4.2~ 2.75V is at least 115mAh/g, an energy density of the positive electrode is at least 345mAh/ cm^3 (the energy density of the positive electrode mAh/ cm^3= the compact density of the positive electrode g/cm^3 x the initial capacity mAh/g), an circulation capacity retention of charging and discharging 1C at 55 °C is at least 80%, an over load charge of 1C at 10V does not result in an explosion nor a burning, a circulation life span at 25 °C is at least 1 000 times, a capacity is maintained at least 80%, a capacity of charging 1C with a charging voltage of 4.3V is at least 135mAh/g, a capacity of charging 1C with a charging voltage of 4.4V is at least 140mAh/g, the processability is good and the anode material pole piece is not easy to slip off.

[0051] The negative electrode is consisted of negative current collector and active cathode material coated on the negative current collector, the separator is just a solid insulation layer or conductive solid matter, so that the positive electrode is separated from the negative electrode. The container is used for receiving the positive electrode, the negative electrode, the separator, and the electrolytic solution.

[0052] The anode material of the battery of the present invention is prepared by the following steps: mix $Li_wMn_x(CoNi)_yO_z$, electric conductive carbon black which is 2.0~ 3.0% weight of the anode material, and binder PVDF which is 2.0~2.5% weight of the anode material to obtain a resulting mixture, add n-methyl pyrrolidone thereto with a ratio of the resulting mixture to n-methyl pyrrolidone is 1:0.9 by weight, after uniformly stirring to obtain a broth, coat the broth onto the aluminum foil current collector, dry and compressing to obtain the anode material pole piece. The cathode material is prepared by the following steps: mix active negative cathode material which is mesocarbon microbeads, conductive agent S-P which is 2% weight of the cathode material, and binder PVDF which is 2.0~2.5% weight of the cathode material to obtain a resulting mixture, add n-methyl pyrrolidone thereto with a ratio of the resulting mixture to n-methyl pyrrolidone is 1:1 by weight, after uniformly stirring to obtain a broth, coat the broth onto the copper foil current collector, dry and compress to obtain the cathode material pole piece. The separator is made of PPPE complex material, the container comprises an aluminum casing with an insulation layer and a battery lid with lead guiding holes. The compressed anode material pole piece and the cathode material pole piece is welded with leads, and then the separator is inserted therebetween, after winding on a up-coiler, the resulting assembly is put into the aluminum casing, then the leads are guided out of the battery lid, and then the lead guiding holes are sealed by glue. The battery lid and the aluminum casing are sealedly welded together. The electrolytic solution is injected thereinto in an environment with a moisture lower than 1.5%, the electrolytic solution is a mixture of EC, DEC, and DMC with a mass ratio of 1:1:1, the electrolyte is 1M lithium hexafluorophosphate, and the container is immediately sealed after the injection process, a battery type is square 053084.

[0053] The charging and discharging test of the lithium ion power battery is carried out according to the testing method of GB/T18287-2000, the testing device is a BS-9360 battery testing cabinet of Guangzhou Qingtian Co., Ltd.

[0054] 1) Preparing of a precursor and sintering of a monocrystalline.

[0055] Example 1

[0056] Lithium carbonate solution containing 0.3 mol Li was dispersed in 300ml 2 wt %,polyethylene glycol hydrophilic colloid solution, stirring at a speed of 50rin/min for 10min to obtain a colloid product, nickel carbonate with 0.1mol Ni and manganese carbonate with 0.8 mol Mn were added thereto, stirring at a speed of 60rin/min for 10min, drying at 150 °C for 10 hours, and stirring at a speed 3000rin/min for 2min to yield a precursor 1 of crystalline of Li with Ni and Mn

[0057] The precursor 1 was sintered at 850°C for 7 hours, after natural cooling, and cutting a particle size thereof to D50=12μm so as to obtain the monocrystalline compound which wss $LiMn_{2n}Ni_{2(1-n)}O_4$, wherein n<1, so that a monocrystalline A was yielded. An x ray diffraction pattern showed that the monocrystalline A was of a spinel structure, as shown in Fig. 1. A scanning electron micrograph suggested that the monocrystalline A is of a single crystalline composition, as shown in Fig. 2.

[0058] Example 2

[0059] Lithium hydroxide solution containing 1 mol Li was dispersed in 300ml 5 wt % polyethylene glycol hydrophilic colloid solution, stirring at a speed of 60rin/min for 70min to obtain a colloid product, cobalt oxalate with 0.1mol Co , nickel oxalate with 0.45 mol Ni and mangous oxalate with 0.45mol Mn were added thereto, stirring at a speed of 50rin/min for 10min, drying at 450 °C for 10 hours, and stirring at a speed 3000rin/min for 2min to yield a precursor 2 of crystalline of Li with Ni , Co and Mn.

[0060] The precursor 2 was sintered at 920 °C for 10 hours, after natural cooling to a room temperature, and cutting a particle size thereof to D50=18μm so as to obtain the monocrystalline compound which was $LiCO_n(NiMn)_{1-n}O_2$, wherein $n < 1$, so that a monocrystalline B was yielded. An x ray diffraction pattern showed that the monocrystalline B was of a layered structure, as shown in Fig. 3. A scanning electron micrograph suggested that the monocrystalline B was of a single crystalline composition, as shown in Fig. 4.

[0061] Example 3

[0062] Lithium carbonate solution containing 0.3 mol Li was dispersed in 200ml 4 wt % polyethylene glycol hydrophilic colloid solution, stirring at a speed of 50rin/min for 120min to obtain a colloid product, nickel carbonate with 0.06 mol Ni, and manganese carbonate with 1.0 mol Mn were added thereto, stirring at a speed of 50rin/min for 20min, drying at 250 °C for 10 hours, and stirring at a speed 2000rin/min for 15min to yield a precursor 3 of crystalline of Li with Ni and Mn

[0063] The precursor 3 was sintered at 750°C for 15 hours, after natural cooling to a room temperature, and cutting a particle size thereof to D50=8μm so as to obtain the monocrystalline compound which was $LiMn_{2n}Ni_{2(1-n)}O_4$, wherein $n < 1$, so that a monocrystalline C was yielded. An x ray diffraction pattern showed that the monocrystalline C was of a spinel structure, as shown in Fig. 5. A scanning electron micrograph suggested that the monocrystalline C was of a single crystalline composition, as shown in Fig. 6.

[0064] Example 4

[0065] Lithium carbonate solution containing 0.6 mol Li was dispersed in 250ml 3 wt % polyethylene glycol hydrophilic colloid solution, stirring at a speed of 55rin/min for 100min to obtain a colloid product, nickel carbonate with 0.6 mol Ni, and manganese carbonate with 0.4 mol Mn were added thereto, stirring at a speed of 55rin/min for 10min, drying at 600°C for 2 hours, and stirring at a speed 1500rin/min for 30min to yield a precursor 4 of crystalline of Li with Ni and Mn

[0066] The precursor 4 was sintered at 1000 °C for 4 hours, after natural cooling to a room temperature, and cutting a particle size thereof to D50=16μm so as to obtain the monocrystalline compound which was $LiNi_nMn_{1-n}O_2$, wherein $n < 1$, so that a monocrystalline D was yielded. An x ray diffraction pattern showed that the monocrystalline D was of a layered structure, as shown in Fig. 7. A scanning electron micrograph suggested that the monocrystalline D was of a single crystalline composition, as shown in Fig. 8.

[0067] Example 5

[0068] Lithium carbonate solution containing 1.2 mol Li was dispersed in 200ml 4 wt % polyethylene glycol hydrophilic colloid solution, stirring at a speed of 50rin/min for 90min to obtain a colloid product, nickel carbonate with 0.01 mol Ni, and manganese carbonate with 2.0 mol Mn were added thereto, stirring at a speed of 50rin/min for 30min, drying at 150 °C for 15 hours, and stirring at a speed 2000rin/min for 15min to yield a precursor 5 of crystalline of Li with Ni and Mn

[0069] The precursor 5 was sintered at 800 °C for 15 hours, after natural cooling to a room temperature, and cutting a particle size thereof to D50=8μm so as to obtain the monocrystalline compound which was $LiMn_2Ni_{2(1-n)}O_4$, wherein $n < 1$, so that a monocrystalline E was yielded. An x ray diffraction pattern showed that the monocrystalline E was of a spinel structure, as shown in Fig. 9. A scanning electron micrograph suggested that the monocrystalline E was of a single crystalline composition, as shown in Fig. 10.

[0070] 2) Synthesizing of polycrystalline,

[0071] Example 6

[0072] Monocrystalline A and monocrystalline B at a mol ratio of Mn to Co plus Ni plus Mn was 73.7:100 were mixed and stirred at a speed of 100rin/min for 20min to obtain a mixture, aluminum acetate containing 0.01mol Al which was dissolved in 100ml 50 wt % ethanol aqueous solution was then added to the mixture, stirring at a speed of 100 rin/min for 30min, drying at 100 °C for 10 hours, heating with a heating rate of 100°C/hr until a temperature thereof amounted to 850°C, and activating for 2 hours, so that crystalline textures were in a symbiotic or mixed phase. The crystalline textures in a symbiotic or mixed phase were grinded at a rotating speed of 1500rin/min for 5min to yield the high manganese anode material. Referring to Fig. 9 of the drawing, an x ray diffraction pattern showed that the crystalline textures were symbiotic $LiMn_{2n}Ni_{2\,(1-n)}\,O_4$/. $LiCo_n\,(NiMn)\,_{1-n}O_2$, an ionic radius of Al^{3+} was 0.0535nm and was smaller than an ionic radius of Li^{1+} which was 0.076nm, so that part of the Li^+ was replaced in a dynamic condition. And thus the Li^{1+} of the monocrystallines and other crystalline in different phases were further dispersed. The characteristic peaks of the x ray diffraction pattern showed that the crystalline structure was different from a simple mixed polycrystalline, the characteristic peak 003 and the characteristic peak 111 were substantially overlapped, indicating that the crystalline textures are in a symbiotic phase. Referring to Fig. 10 of the drawing, the scanning electron micrograph suggested an existence of different crystalline textures instead of a single monocrystalline.

[0073] The high manganese polycrystalline material of example 6 was used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0074] Example 7

[0075] Monocrystalline A, monocrystalline B and monocrystalline C at a mol ratio of Mn to Co plus Ni plus Mn was 69.4:100 were mixed and stirred at a speed of 150rin/min for 5min to obtain a mixture, magnesium acetate containing 0.1mol Mg which was dissolved in 100mol 30 wt % ethanol aqueous solution was then added to the mixture, stirring at a speed of 60 rin/min for 60min, drying at 200°Cfor 2 hours, heating with a heating rate of 50°C/hr until a temperature thereof amounted to 650°C, and activating for 5 hours, so that crystalline textures were in a symbiotic or mixed phase. The crystalline textures in a symbiotic or mixed phase were grinded at a rotating speed of 3000rin/min for 2min to yield the high manganese anode material. Referring to Fig. 11 of the drawing, an x ray diffraction pattern showed that the crystalline textures were symbiotic $LiMn_{2n}Ni_{2\,(1-n)}\,O_4$/ $LiCo_n\,(NiMn)_{\,1-n}O_2$/ $LiMn_{2n}Ni_{2\,(1-n)}\,O_4$, an ionic radius of $Mg^{2+}$was 0.072nm and was smaller than an ionic radius of Li^{1+} which was 0.076nm, so that part of the Li^{1+} was replaced in a dynamic condition. And thus the Li^{1+} of the monocrystallines and other crystalline in different phases were further dispersed. The characteristic peaks of the x ray diffraction pattern showed that the crystalline structure was different from a simple mixed polycrystalline, the characteristic peak 003 and the characteristic peak 111 were substantially overlapped, indicating that the crystalline textures are in a symbiotic phase. Referring to Fig. 12 of the drawing, the scanning electron micrograph suggested an existence of different crystalline textures instead of a single monocrystalline.

[0076] The high manganese polycrystalline material of example 7 was used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0077] Example 8

[0078] Monocrystalline C and monocrystalline D at a mol ratio of Mn to Co plus Ni plus Mn was 60.3:100 were mixed and stirred at a speed of 120rin/min for 10min to obtain a mixture, aluminum acetate containing 0.01 mol Al which was dissolved in 300ml 60 wt % ethanol aqueous solution was then added to the mixture, stirring at a speed of 70 rin/min for 40min, drying at 110°Cfor 10 hours, heating with a heating rate of 70°C/hr until a temperature thereof amounted to 300°C, and activating for 7 hours, so that crystalline textures were in a symbiotic or mixed phase. The crystalline textures in a symbiotic or mixed phase were grinded at a rotating speed of 2000rin/min for 3min to yield the high manganese anode material. Referring to Fig. 13 of the drawing, an x ray diffraction pattern showed that the crystalline textures were symbiotic $LiMn_{2n}Ni_{2\,(1-n)}\,O_4/LiNi_nMn_{1-n}O_2$, an ionic radius of $Al^{3+}$was 0.0535nm and was smaller than an ionic radius of Li^{1+} which was 0.076nm, so that part of the Li^{1+} was replaced in a dynamic condition. And thus the Li^{1+} of the monocrystallines and other crystalline in different phases were further dispersed. The characteristic peaks of the x ray diffraction pattern showed that the crystalline structure was different from a simple mixed polycrystalline, the characteristic peak 003 and the characteristic peak 111 were substantially overlapped, indicating that the crystalline textures are in a symbiotic phase. Referring to Fig. 14 of the drawing, the scanning electron micrograph suggested an existence of different crystalline textures instead of a single monocrystalline.

[0079] The high manganese polycrystalline material of example 8 was used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0080] Example 9

[0081] Monocrystalline A, monocrystalline B and monocrystalline D at a mol ratio of Mn to Co plus Ni plus Mn was 80.3:100 were mixed and stirred at a speed of 135rin/min for 10min to obtain a mixture, $Cr(CH_3COO)_3$ containing 0.06mol Cr which was dissolved in 100mol 50 wt % ethanol aqueous solution was then added to the mixture, stirring at a speed of 90 rin/min for 50min, drying at 190°C for 3 hours, heating with a heating rate of 85°C/hr until a temperature thereof amounted to 500°C, and activating for 3 hours, so that crystalline textures were in a symbiotic or mixed phase. The crystalline textures in a symbiotic or mixed phase were grinded at a rotating speed of 1600rin/min for 3min to yield the high manganese anode material. Referring to Fig. 15 of the drawing, an x ray diffraction pattern showed that the crystalline textures were symbiotic $LiMn_{2n}Ni_{2\,(1-n)}\,O_4/LICo_n(NiMn)_{1-n}O_2/\ LiNi_nMn_{1-n}O_2$, an ionic radius of Cr^{3+} was 0.0615nm and was substantial equal to an ionic radius of Mn^{3+} which was 0.064nm, so that part of the Li^{1+} was replaced in a dynamic condition. And thus the Li^{1+} of the monocrystallines and other crystalline in different phases were further dispersed. The characteristic peaks of the x ray diffraction pattern showed that the crystalline structure was different from a simple mixed polycrystalline, the characteristic peak 003 and the characteristic peak 111 were substantially overlapped, indicating that the crystalline textures were in a symbiotic phase. Referring to Fig. 16 of the drawing, the scanning electron micrograph suggested an existence of different crystalline textures instead of a single monocrystalline.

[0082] The high manganese polycrystalline material of example 9 was used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0083] Example 10

[0084] Monocrystalline B and monocrystalline C at a mol ratio of Mn to Co plus Ni plus Mn was 89.2:100 were mixed and stirred at a speed of 140rin/min for 20min to obtain a mixture, $Zr(NO_3)_4$ containing 0.06mol Zr which was dissolved in 100ml 50 wt % ethanol aqueous solution was then added to the mixture, stirring at a speed of 85 rin/min for 45min, drying at 150°Cfor 3 hours, heating with a heating rate of 100°C/hr until a temperature thereof amounted to 600°C, and activating for 4 hours, so that crystalline textures were in a symbiotic or mixed phase. The crystalline textures in a symbiotic or mixed phase were grinded at a rotating speed of 1500rin/min for 5min to yield the high manganese anode material. Referring to Fig. 17 of the drawing, an x ray diffraction pattern showed that the crystalline textures were symbiotic $LiCo_n(NiMn)_{1-n}O_2/LiMn_{2n}Ni_{2\,(1-n)}\,O_4$, an ionic radius of Zr^{4+} was 0.072nm and was substantial equal to an ionic radius of Mn^{3+} which was 0.064nm, so that part of the Li^{1+} was replaced in a dynamic condition. And thus the Li^{1+} of the monocrystallines and other crystalline in different phases were further dispersed. The characteristic peaks of the x ray diffraction pattern showed that the crystalline structure was different from a simple mixed polycrystalline, the characteristic peak 003 and the characteristic peak 111 were substantially overlapped, indicating that the crystalline textures were in a symbiotic phase. Referring to Fig. 18 of the drawing, the scanning electron micrograph suggested an existence of different crystalline textures instead of a single monocrystalline.

[0085] The high manganese polycrystalline material of example 10 was used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0086] Accordingly, in example 1 to example 5, compound of Co, Ni and Mn had used carbonate slat thereof. Hydroxy compound and oxalate slat of Co, Ni and Mn had substantial same physical and chemical property with the carbonate salt. Element Co, Ni, and Mn all belonged to transition elements and had substantial approximate ionic radius which was 0.053~0.06nm, and an ion valence was the same which was +2, so that a harmony mixed crystalline structure was formed. And thus a chemical environment for the dispersing of Li^+ to disperse was provided, making a great a contribution to a formation of a basic crystalline frame for the preparing of the precursor of Li with Co, Ni and Mn. Therefore, hydroxy compound and oxalate slat of Co, Ni and Mn were suitable to be employed in preparing the precursor of Li with Co, Ni and Mn.

[0087] Accordingly, in example 6 to example 10, element Al and Mg were taken as examples of the doping element. Element Si, Ti, Fe, and Zr, which were like Al and Mg, had an ionic radius of 0.04~0.067nm and was smaller than an ionic radius of Li^+ which was 0.076nm, and was substantial approximate to the ionic radius of Mn^{3+} which was 0.0645nm, so that Li^+ could be replaced and formation of the crystalline textures was ensured under certain dynamic condition. Adding doping element could inhibit a disproportionation of Mn^{3+} to Mn^{2+} and Mn^{4+}. Providing at least one doping element could inhibit phase change and balance the electric charge between the different crystalline phases, so that a high temperature durability of the material was enhanced, a self discharge thereof was reduced, and security property such as thermal stability was enhanced.

[0088] Control Example 1

[0089] Referring to Fig. 19 of the drawing, the control example 1 was a public sold lithium iron phosphate ZHFe1# anode material of Shenzhen Zhenhua Chene-Chem Co., Ltd. An x ray diffraction pattern showed that the crystalline structure was a single lithium iron phosphate olivine structure. Referring to Fig. 20 of the drawing, a scanning electron micrograph showed that a particle size of the monocrystalline was smaller than 1μm and the monocrystalline was evenly distributed. This anode material was also used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0090] Control Example 2

[0091] Referring to Fig. 21 of the drawing, the control example 1 was a public sold lithium manganate ZHM01# anode material of Shenzhen Zhenhua Chene-Chem Co., Ltd. An x ray diffraction pattern showed that the crystalline structure was a single lithium manganate spinel structure. Referring to Fig. 22 of the drawing, a scanning electron micrograph showed that a particle size of the monocrystalline was smaller than 1μm and the monocrystalline was in a reunion state. The specific surface area which was 0.6~ 0.9 m^2/g was relatively smaller, This anode material was also used as an active anode material to prepare a 053048 square type lithium ion battery, the performance and electric property of the anode material pole piece was shown in Table 1.

[0092] Conclusion: the high manganese polycrystalline material of the present invention had a compact density ($3.0{\sim}3.5g/cm^3$) lager than a compact density of the lithium manganate ($2.9{\sim}3.3g/cm^3$) and a compact density of the lithium iron phosphate ($2.1\ {\sim}2.5g/cm^3$); a capacity (≥115mAh/g) higher than the a capacity of lithium manganate (95~110mAh/g) and lower than a capacity of the lithium iron phosphate (~130mAh/g. We could make a conclusion that the high manganese polycrystalline material of the present invention had an energy density larger than an energy density of the lithium manganate and the lithium iron phosphate. For the olivine lithium iron phosphate, an electric potential, which was 3.4V(vs.Li/Li+), was relatively low, a particle size of the monocrystalline was relatively small (≤1um), a specific surface area was relatively large ($12{\sim}20cm^2/g$), a tap density was relatively low(≤1.2g/cm3), so that a tap density and an energy density of the pole piece were relatively low. For the spinel lithium mangnate, the ternary Li—Mn—O combination was easy to form various kinds of compound and also could be transformed into each other under different conditions. As a result, the crystalline structure was easy to change its pattern during charging and discharging process, and the capacity was decayed fast. But the high manganese polycrystalline material of the present invention had overcome the disadvantages of the lithium mangnate structure resulting from the existence of mulit-element and polycrystalline. Therefore, the capacity and stability of the high manganese polycrystalline material of the present invention were both higher than lithium manganate. In addition, the safety was substantially the same as lithium mangnate and lithium iron phosphate, the circulation performance at high temperature was substantially the same as lithium iron phosphate but greatly better than lithium mangnate, the circulation performance at normal temperaturewas substantially the same as lithium iron phosphate but better than lithium mangnate. In view of the above, the high manganese polycrystalline material of the present invention had a good performance in regard of the energy density and the safety, so that the high manganese polycrystalline material of the present invention was a perfect choice for the power battery.

[0093] Table 1 showed the testing result of example 5-9 and control example 1-2. The type of the battery was 053084. The charging and discharging voltage was 4.2~2.75V, and the samples of example 5-9 and control example 1-2 were tested with a charging/discharging rate of 1C.

[0094] One skilled in the art will understand that the embodiment of the present invention as shown in the drawings and described above is exemplary only and not intended to be limiting.

[0095] It will thus be seen that the objects of the present invention have been fully and effectively accomplished. The embodiments have been shown and described for the purposes of illustrating the functional and structural principles of the present invention and is subject to change without departure from such principles. Therefore, this invention includes all modifications encompassed within the spirit and scope of the following claims.

Table 1

	Item						
Anode material	Compact density of pole piece (g/cm3)	Initial capacity (mAh/g)	Energy density of positive electrod e (mAh/cm3)	Capacity retention after 300 circles at 25 °C (100%)	Capacity retention after 1000 circles at 25 °C (100%)	Capacity retention after 500 circles at 55 °C (100%)	Over charge experiment at 10V under rate of 1C
Example 6 $LiMn_{2n}Ni_{2(1-n)}O_4$/ $LiCo_n(NiMn)_{1-n}O_2$	3.2	126.2	403.84	91.4	82.4	83.0	Does not burn nor explode
Example 7 $LiMn_{2n}Ni_{2(1-n)}O_4$/ $LiCo_n(NiMn)_{1-n}O_2$/ $LiMn_{2n}Ni_{2(1-n)}O_4$	3.3	126.5	417.45	93.8	85.2	82.2	Does not burn nor explode
Example 8 $LiMn_{2n}Ni_{2(1-n)}O_4$/ $LiNi_nMn_{1-n}O_2$	3.1	117.2	363.32	92.5	83.1	86.4	Does not bum nor explode
Example 9 $LiMn_{2n}Ni_{2(1-n)}O_4$/$LICo_n(NiMn)_{1-n}O_2$/ $LiNi_nMn_{1-n}O_2$	3.2	125.0	400.00	93.8	83.3	82.3	Does not bum nor explode
Example 10 $LiCo_n(NiMn)_{1-n}O_2$/ $LiMn_{2n}Ni_{2(1-n)}O_4$	3.0	118.2	354.60	95.1	85.3	84.8	Does not bum nor explode

(continued)

	Item						
Anode material	Compact density of pole piece (g/cm3)	Initial capacity (mAh/g)	Energy density of positive electrod e (mAh/c m3)	Capacity retention after 300 circles at 25 °C (100%)	Capacity retention after 1000 circles at 25 °C (100%)	Capacity retention after 500 circles at 55 °C (100%)	Over charge experim ent at 10V under rate of 1C
Control example 1 $LiFePO_4$	2.4	130.8	313.92	95.7	90.2	88.7	Does not bum nor explode
Control example 2 $LiMn_2O_4$	3.0	104.6	313.80	90.3	73.1	65.5	Does not bum nor explode

Claims

1. A high manganese polycrystalline anode material of the formula: $Li_wMn_x(CoNi)_yO_z$, wherein x=0.4~2.0, y=0.1 ~0.6, x+y<2, z≥2, W≥1, wherein weight of Mn is at least 40% weight of $Li_wMn_x(CoNi)_yO_z$, particle size thereof is 7~20μm, wherein said high manganese polycrystalline anode material is consisted of at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n$ (NiMn) $_{1-n}O_2$, $LiNi_{0.8}$ $Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)}O_4$ and $LiNiO_2$, wherein n<1, and said crystalline textures are in a symbiotic and mixed phase.

2. The high manganese polycrystalline anode material , as recited in claim 1, wherein a mole percentage of Mn is 60~90% of Co, Ni plus Mn

3. The high manganese polycrystalline anode material , as recited in claim 2, wherein a doping element in lattice of said crystalline textures is selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr, wherein a doping amount is 0.01 ~0.1 mol/mol $Li_wMn_x(CoNi)_yO_z$.

4. A method of preparing of a high manganese polycrystalline anode material, said method comprises the following steps:

   1) preparing of a precursor: dispersing of 0.3 ~ 1.2 mol Li_2CO_3, LiAc or LiOH in 200~300ml 2~5 wt % polyethylene glycol hydrophilic colloid solution, stirring at a speed of 10 ~ 60rin/min for 50 ~ 120min to obtain a colloid product, adding compound of Co, Ni and Mn thereto with a mol ratio of Mn to Ni plus Co is 0.4~2.0: 0.01 ~ 0.6, stirring at a speed of 50~60rin/min for 10~30min, drying at 150~600°C for 2~15 hours, and stirring at a speed 1500~3000rin/min for 2~30min to obtain said precursor of crystalline of Li with Co, Ni and Mn;
   2) sintering of a monocrystalline: sintering said precursor at 750~1000°C for 4~15 hours, cooling, and cutting a particle size thereof to D50=7~20μm so as to obtain the monocrystalline compound which is selected from the group consisting of $LiMn_2O_4$, LiCon (NiMn) $_{1-n}O_2$, $LiNi_{0.8}$ $Co_{0.2}O2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2\,(1-n)}$ O_4 and $LiNiO_2$, wherein n < 1; and
   3) synthesizing of polycrystalline: mixing at least two of said monocrystalline compounds at a mol ratio of Mn to Co plus Ni plus Mn is 60~90:100, stirring at a speed of 100~150rin/min for 5~20min to obtain a mixture, wherein 0.01~0,1mol soluble salt of a doping element selected from at least one of the group consisting of Al, Si, Ti, Fe, Zr, Mg and Cr dissolved in 100~300ml 30~60 wt % ethanol aqueous solution is added to said mixture, stirring at a speed of 60~100 rin/min for 3~60min, drying at 100~200 °C for 2~10 hours, heating with a heating rate of 50~100 °C/hr until a temperature thereof amounts to 300~850°C, and activating for 2~10 hours, so that crystalline textures are in a symbiotic or mixed phase.

5. The method, as recited in claim 4, wherein said crystalline textures in said symbiotic phase are subjected to a smashing process.

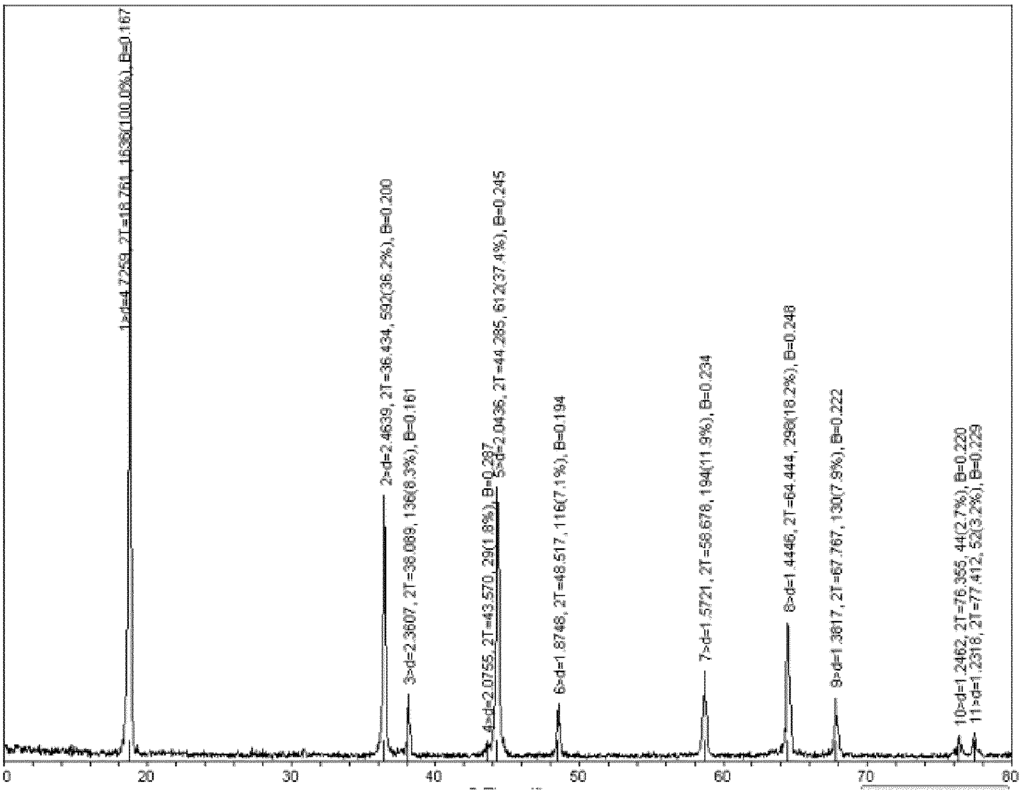
6. The method, as recited in claim 5, wherein said crystalline textures in a symbiotic or mixed phase are grinded at a rotating speed of 1500~3000rin/min for 2~ 5min.

7. The method, as recited in claim 6, wherein said compound of Co, Ni and Mn is selected from the group consisting of monohydroxy compound, oxalate and carbonate of Co, Ni and Mn

8. The method, as recited in claim 7, wherein said precursor is sintered at 750~1000°C for 4~15 hours and then naturally cooled down.

9. A lithium ion power battery having a positive electrode, wherein a current collector of said positive electrode is coated with active anode material, wherein a formula of said active anode material is $Li_wMn_x(CoNi)_yO_z$, wherein x=0.4~2.0, y=0.1~ 0.6, $x+y<2$, $z\geq2$, $W\geq1$, wherein weight of Mn is at least 40% weight of $Li_wMn_x(CoNi)_yO_z$, particle size thereof is 7~20μm, wherein said anode material is consisted of at least two crystalline textures which are selected from the group consisting of $LiMn_2O_4$, $LiCo_n (NiMn)_{1-n}O_2$, $LiNi_{0.8} Co_{0.2}O_2$, $LiCoO_2$, $LiNi_nMn_{1-n}O_2$, $LiMn_{2n}Ni_{2(1-n)}O_4$ and $LiNiO_2$, wherein $n<1$, and said crystalline textures are in a symbiotic or mixed phase.

10. The lithium ion power battery, as recited in claim 9, wherein said anode material is prepared by the following steps: mixing $Li_wMn_x(CoNi)_yO_z$, electric conductive carbon black which is 2.0~3.0% weight of the anode material, and binder PVDF which is 2.0~2.5% weight of the anode material to obtain a resulting mixture, adding n-methyl pyrrolidone thereto with a ratio of the resulting mixture to n-methyl pyrrolidone is 1:0.9 by weight, after uniformly stirring to obtain a broth, coating said broth onto said aluminum foil current collector, drying and compressing to obtain said anode material pole piece.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30
40
50
60
70
80

FIG.1

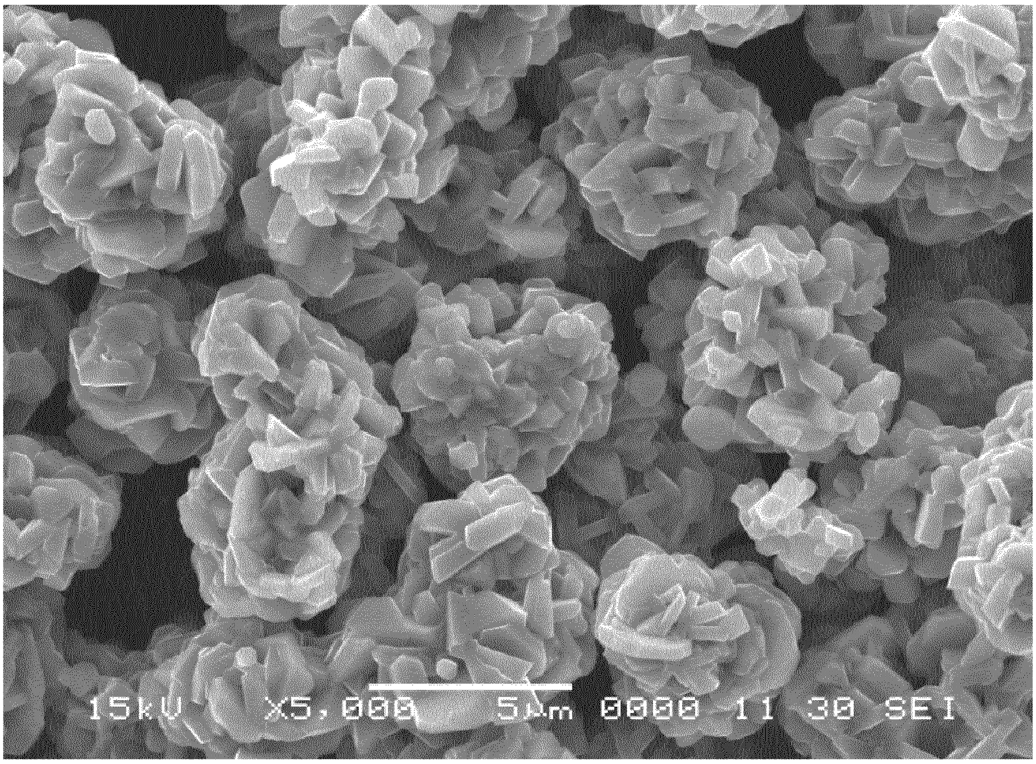
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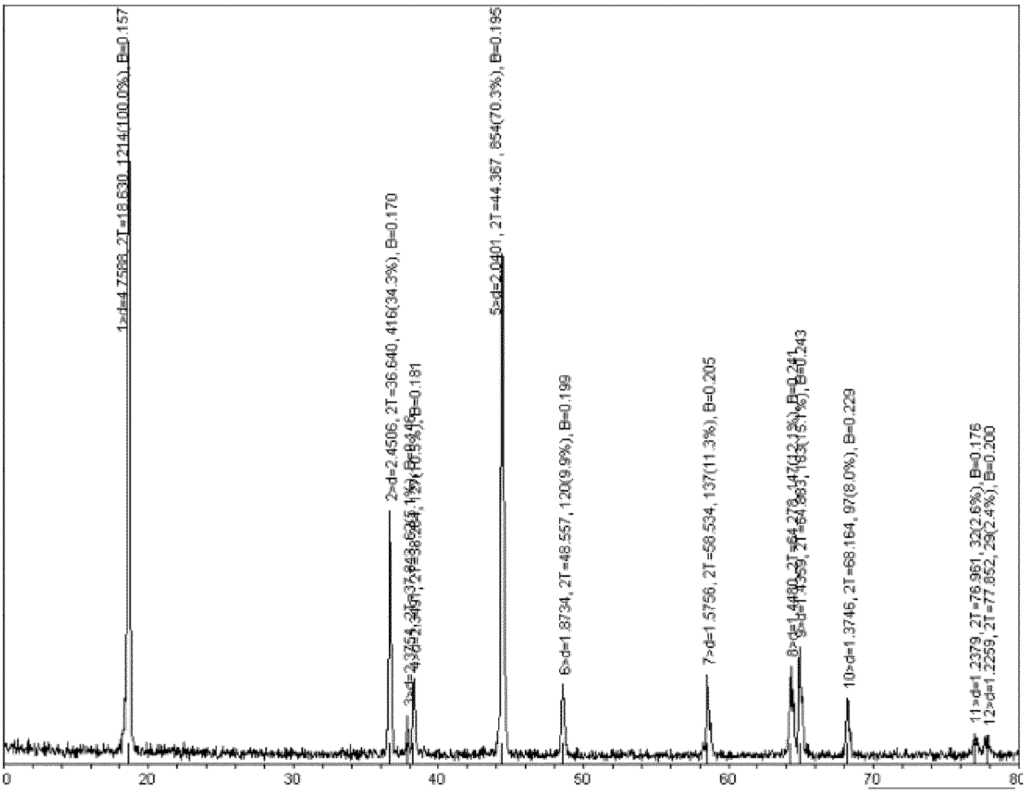
FIG.2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30
40
50
60
70
80

FIG.3

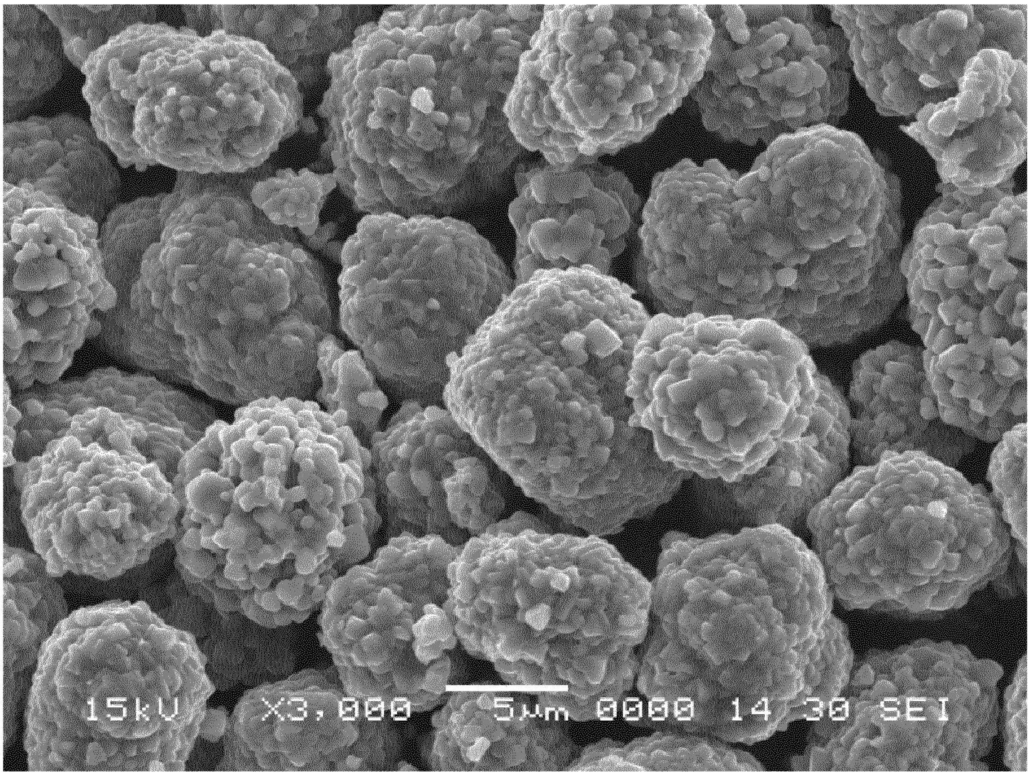
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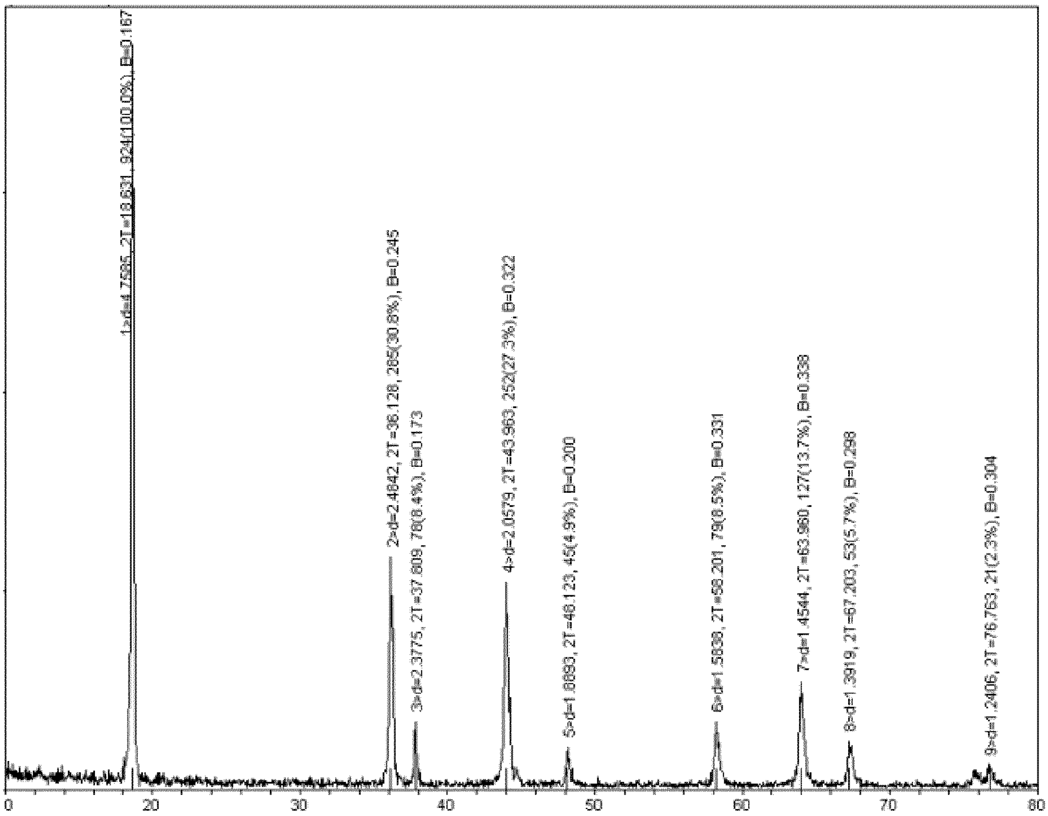
FIG.4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5>d=1.8893, 2T=48.123, 45(4.9%), B=0.200
6>d=1.5838, 2T=58.201, 79(8.5%), B=0.331
7>d=1.4544, 2T=63.960, 127(13.7%), B=0.338
8>d=1.3919, 2T=67.203, 53(5.7%), B=0.298
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40
50
60
70
80

FIG.5

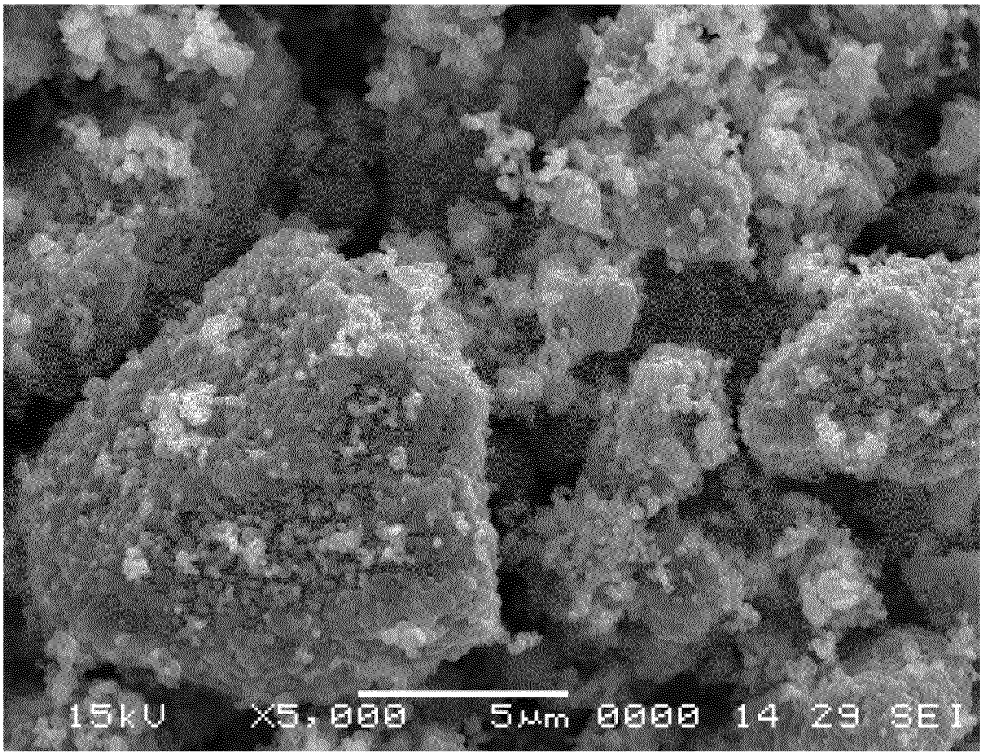
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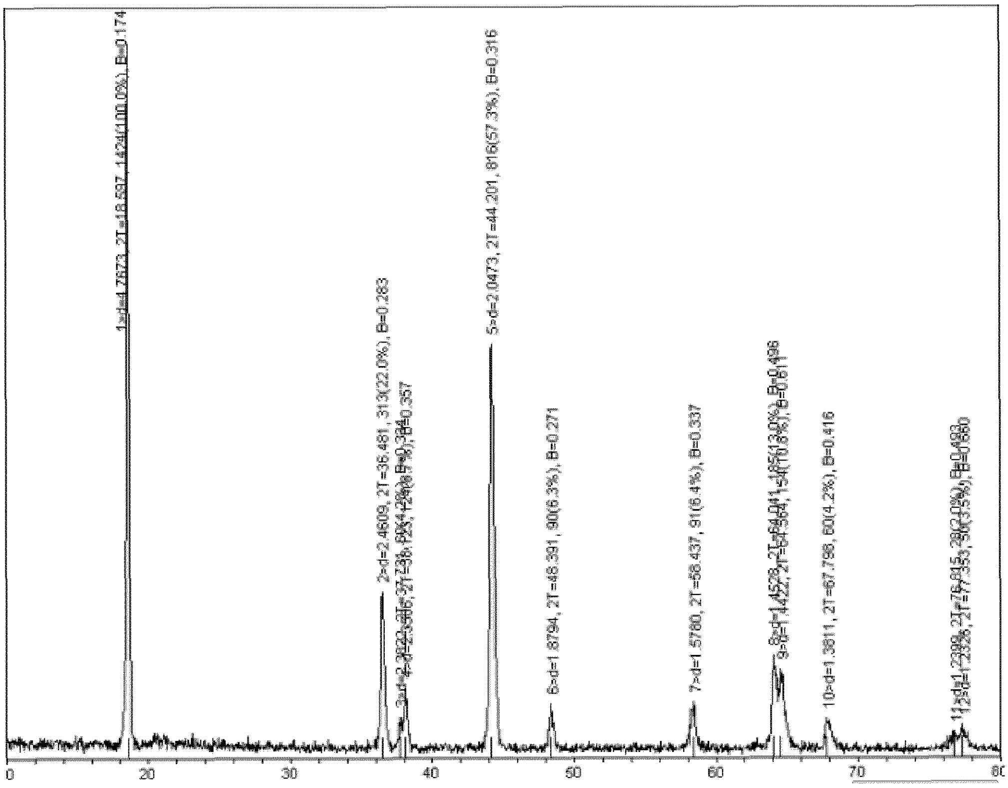
FIG.6


1>d=4.7673, 2T=18.597, 1424(100.0%), B=0.174
2>d=2.4609, 2T=36.481, 313(22.0%), B=0.283
3>d=2.3822, 2T=37.731, 60(4.2%), B=0.334
4>d=2.3586, 2T=38.123, 42(2.9%), B=0.357
5>d=2.0473, 2T=44.201, 816(57.3%), B=0.316
6>d=1.8794, 2T=48.391, 90(6.3%), B=0.271
7>d=1.5780, 2T=58.437, 91(6.4%), B=0.337
8>d=1.4528, 2T=64.041, 185(13.0%), B=0.496
9>d=1.4422, 2T=64.564, 154(10.8%), B=0.611
10>d=1.3811, 2T=67.798, 60(4.2%), B=0.416
11>d=1.2399, 2T=76.815, 28(2.0%), B=0.493
12>d=1.2326, 2T=77.353, 50(3.5%), B=0.660
0
20
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40
50
60
70
8

FIG.7

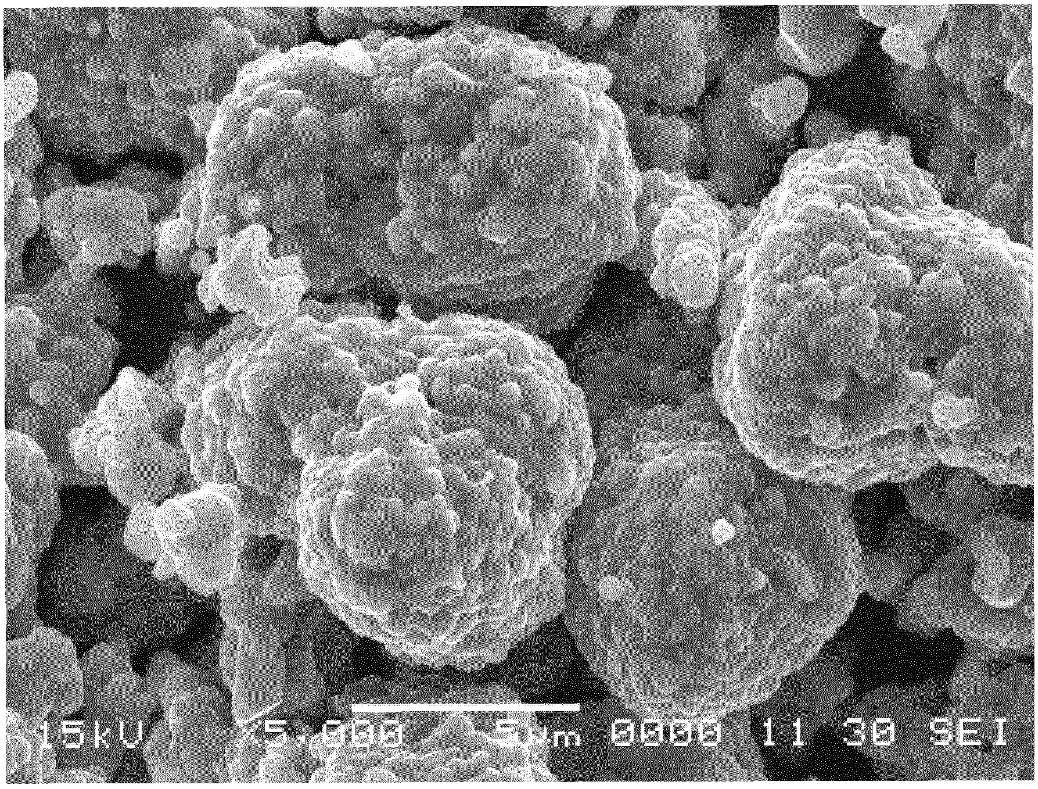
15kV X5,000 5µm 0000 11 30 SEI

FIG.8

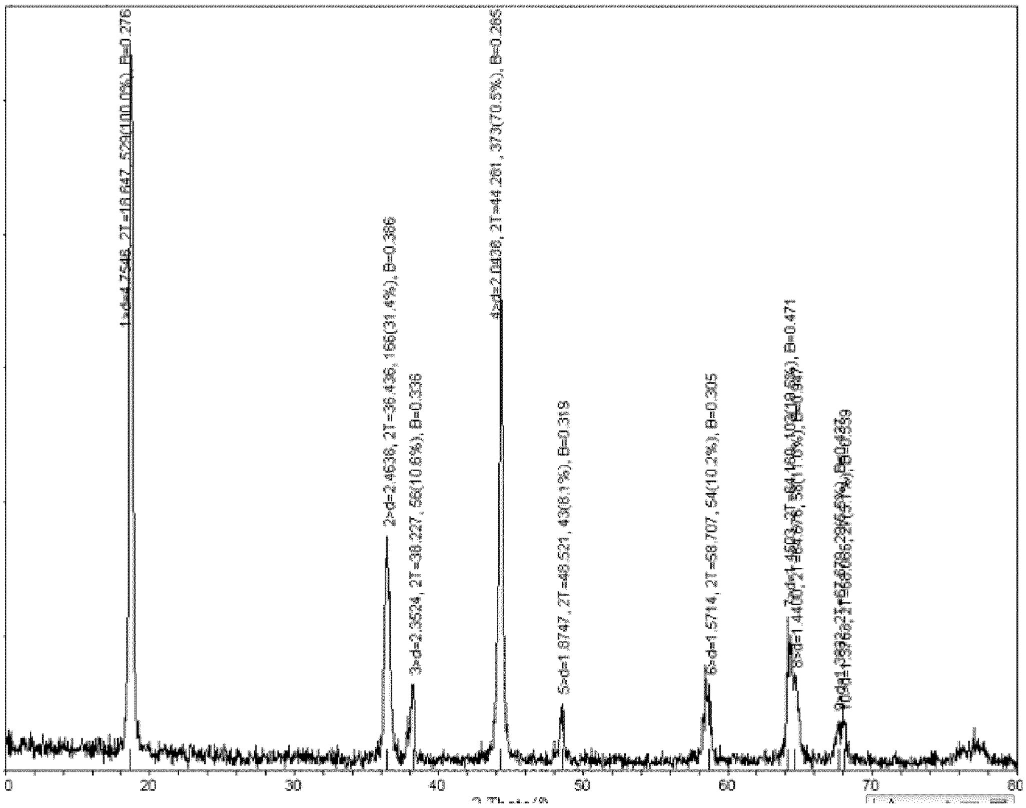
1>d=4.7546, 2T=18.647, 529(100.0%), B=0.276
2>d=2.4638, 2T=36.436, 166(31.4%), B=0.386
3>d=2.3524, 2T=38.227, 56(10.6%), B=0.336
4>d=2.0438, 2T=44.281, 373(70.5%), B=0.265
5>d=1.8747, 2T=48.521, 43(8.1%), B=0.319
6>d=1.5714, 2T=58.707, 54(10.2%), B=0.305
7>d=1.4503, 2T=64.160, 102(19.5%), B=0.471
0
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FIG.9

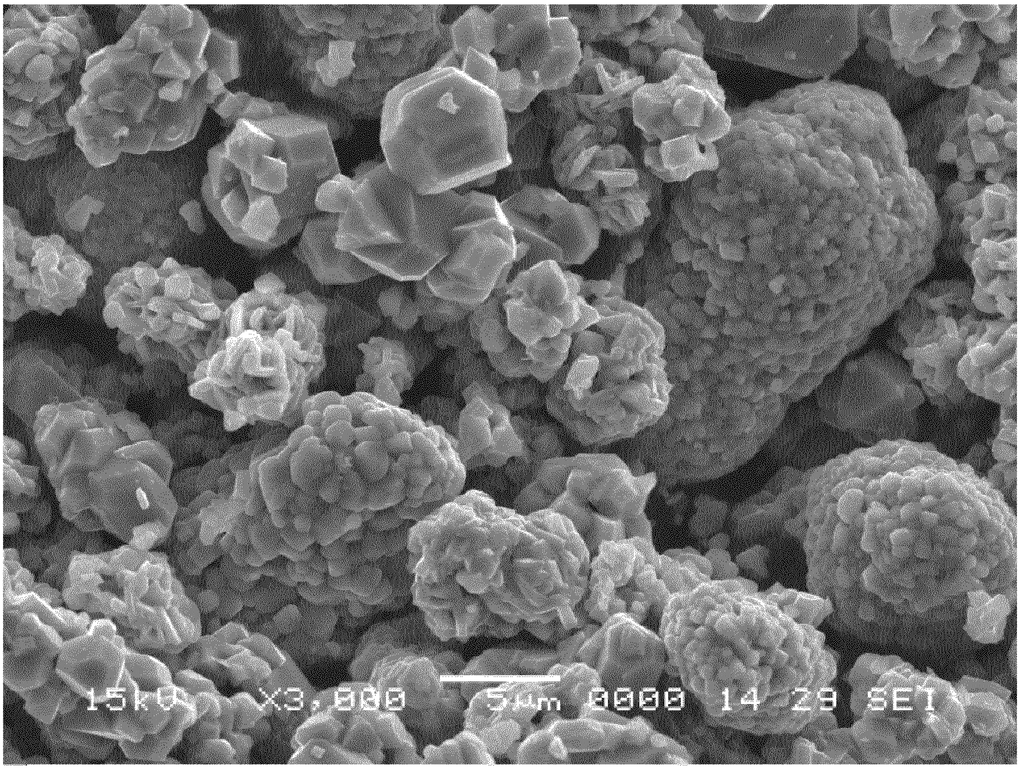
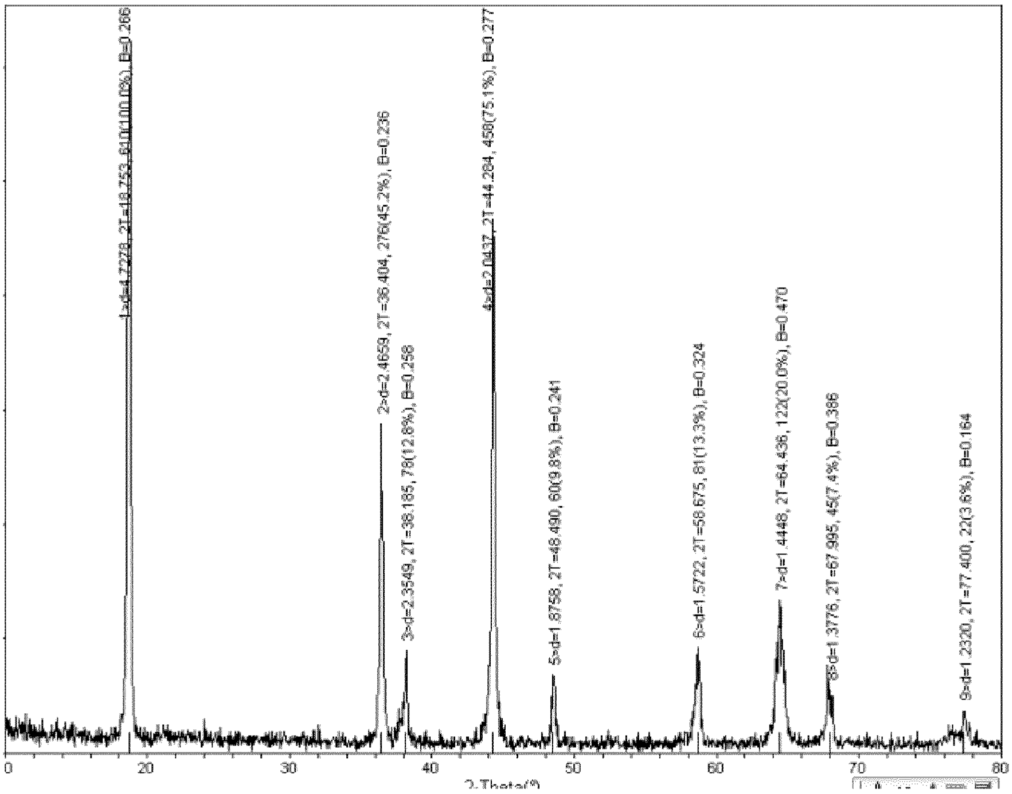

15kV
X3,000
5μm
0000
14 29
SEI

FIG.10


1>d=4.7278, 2T=18.753, 610(100.0%), B=0.266
2>d=2.4659, 2T=36.404, 276(45.2%), B=0.236
3>d=2.3549, 2T=38.185, 78(12.8%), B=0.258
4>d=2.0437, 2T=44.284, 458(75.1%), B=0.277
5>d=1.8758, 2T=48.490, 60(9.8%), B=0.241
6>d=1.5722, 2T=58.675, 81(13.3%), B=0.324
7>d=1.4448, 2T=64.436, 122(20.0%), B=0.470
8>d=1.3776, 2T=67.995, 45(7.4%), B=0.386
9>d=1.2320, 2T=77.400, 22(3.6%), B=0.164
0
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30
40
50
60
70
80
2-Theta(°)

FIG.11

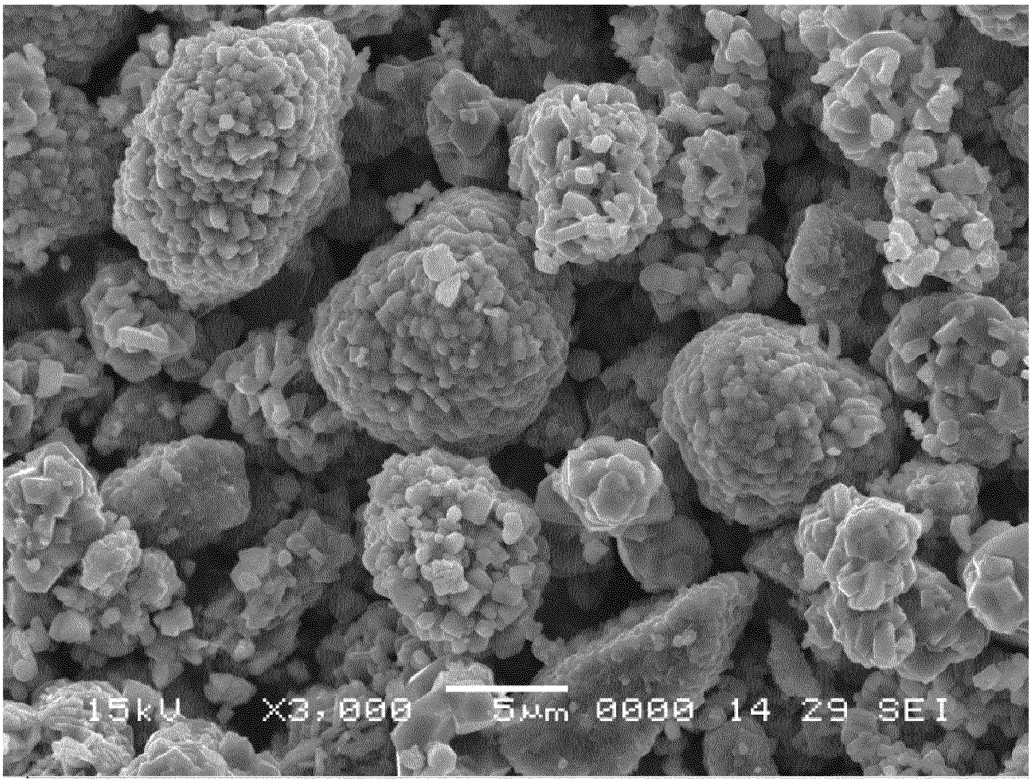
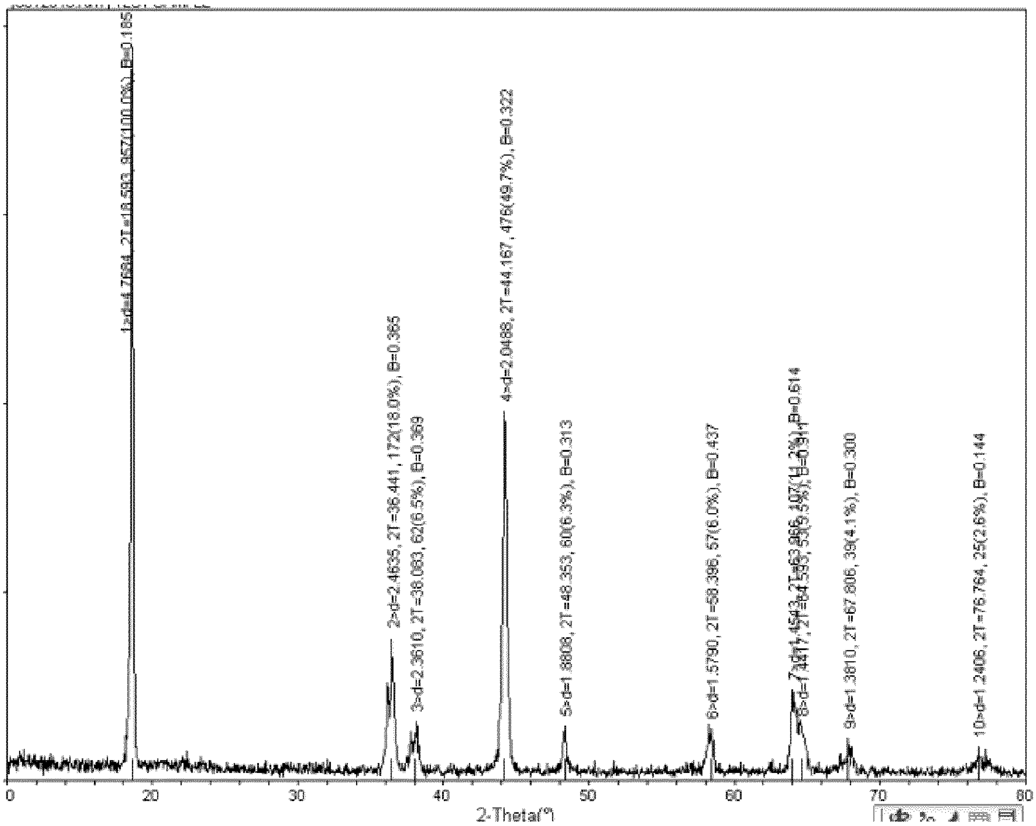

15kV X3,000 5μm 0000 14 29 SEI

FIG.12


1>d=4.7684, 2T=18.593, 957(100.0%), B=0.185
2>d=2.4635, 2T=36.441, 172(18.0%), B=0.365
3>d=2.3610, 2T=38.083, 62(6.5%), B=0.369
4>d=2.0488, 2T=44.167, 476(49.7%), B=0.322
5>d=1.8808, 2T=48.353, 60(6.3%), B=0.313
6>d=1.5790, 2T=58.396, 57(6.0%), B=0.437
7>d=1.4543, 2T=63.966, 107(11.2%), B=0.614
8>d=1.4417, 2T=64.593, 53(5.5%), B=0.91
9>d=1.3810, 2T=67.806, 39(4.1%), B=0.300
10>d=1.2406, 2T=76.764, 25(2.6%), B=0.144
0
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80
2-Theta(°)

FIG.13

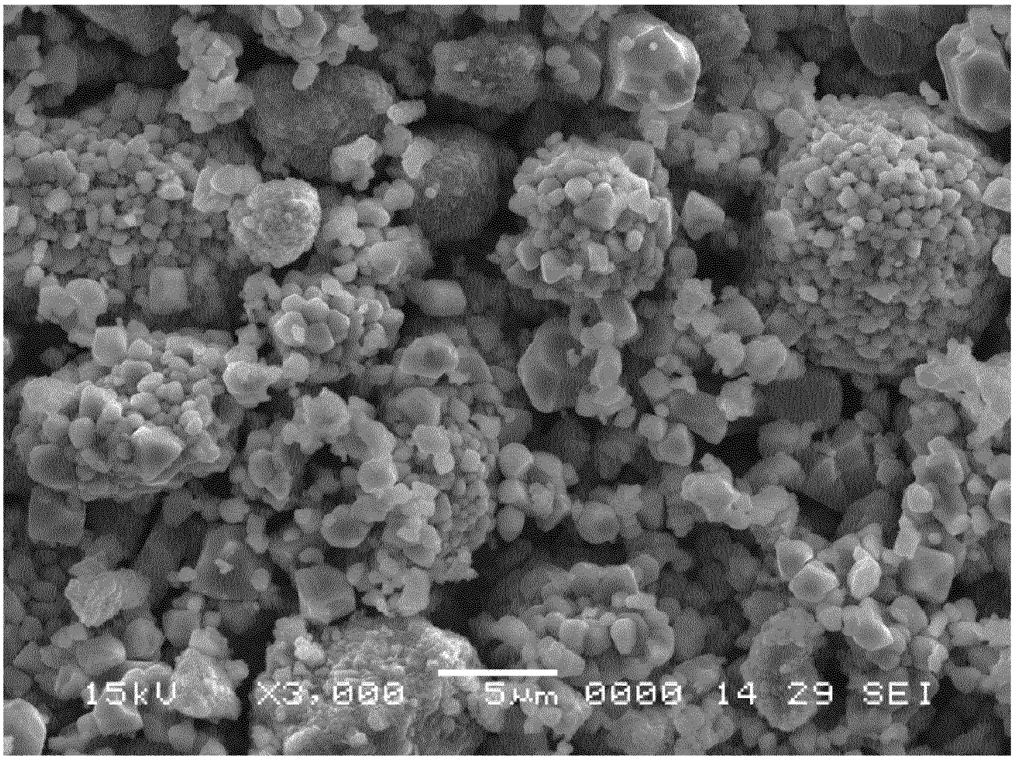
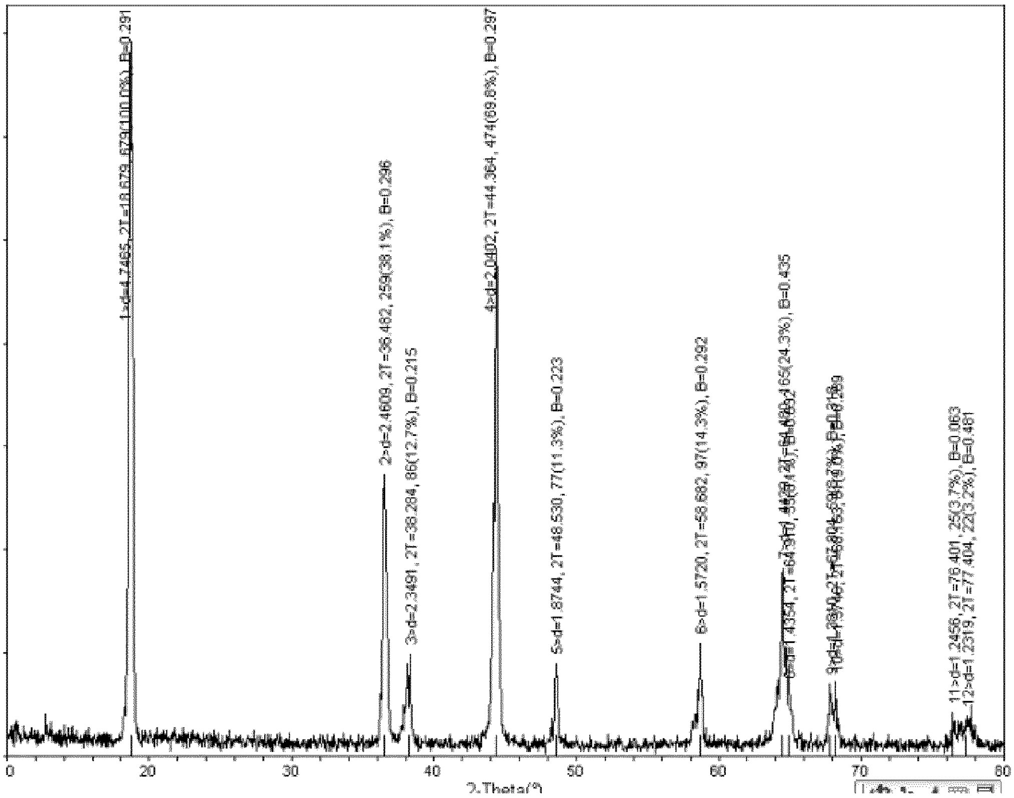

15kV
X3,000
5µm
0000 14 29 SEI

FIG.14


1>d=4.7465, 2T=18.679, 679(100.0%), B=0.291
2>d=2.4609, 2T=36.482, 259(38.1%), B=0.296
3>d=2.3491, 2T=38.284, 86(12.7%), B=0.215
4>d=2.0402, 2T=44.364, 474(69.8%), B=0.297
5>d=1.8744, 2T=48.530, 77(11.3%), B=0.223
6>d=1.5720, 2T=58.682, 97(14.3%), B=0.292
11>d=1.2456, 2T=76.401, 25(3.7%), B=0.063
12>d=1.2319, 2T=77.404, 22(3.2%), B=0.481
0
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70
80
2-Theta(°)

FIG.15

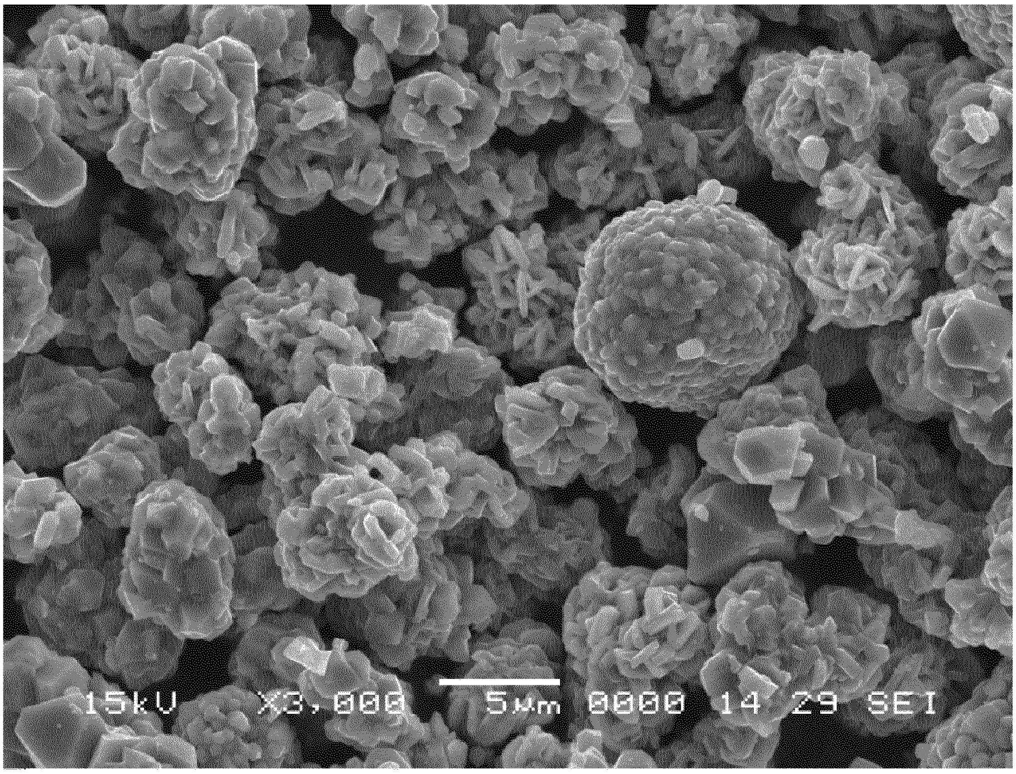
15kV X3,000 5µm 0000 14 29 SEI

FIG.16

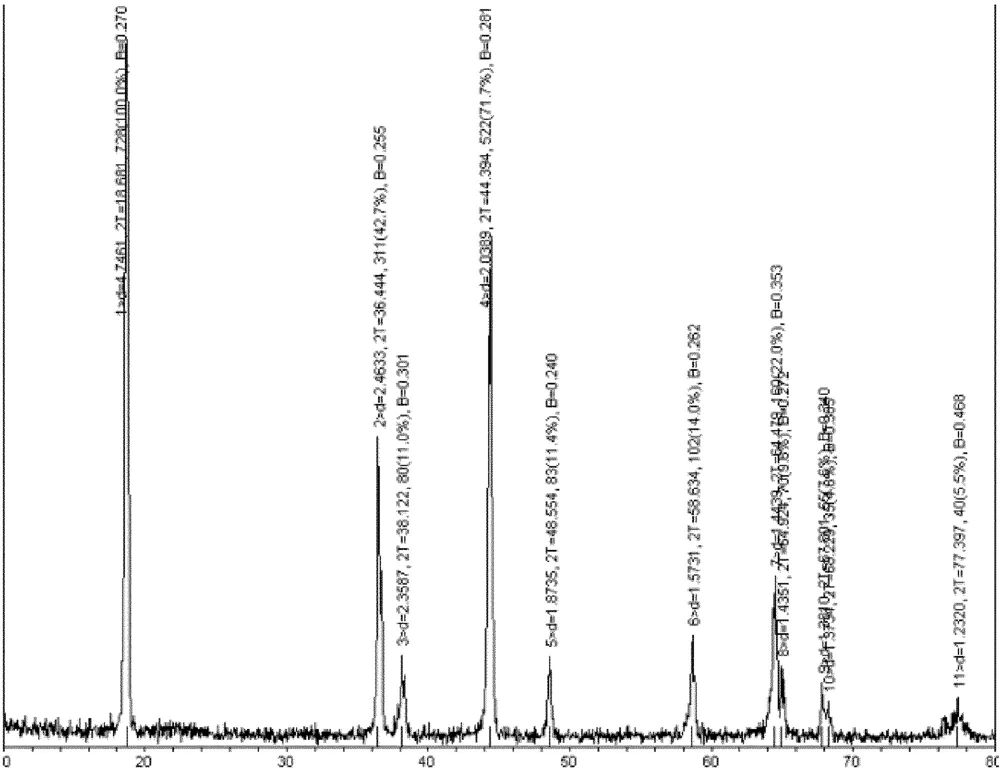
1>d=4.7461, 2T=18.681, 728(100.0%), B=0.270
2>d=2.4633, 2T=36.444, 311(42.7%), B=0.255
3>d=2.3587, 2T=38.122, 80(11.0%), B=0.301
4>d=2.0389, 2T=44.394, 522(71.7%), B=0.281
5>d=1.8735, 2T=48.554, 83(11.4%), B=0.240
6>d=1.5731, 2T=58.634, 102(14.0%), B=0.262
7>d=1.4439, 2T=64.479, 160(22.0%), B=0.353
8>d=1.4351, 2T=64.924, 70(9.6%), B=0.272
11>d=1.2320, 2T=77.397, 40(5.5%), B=0.468
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FIG.17

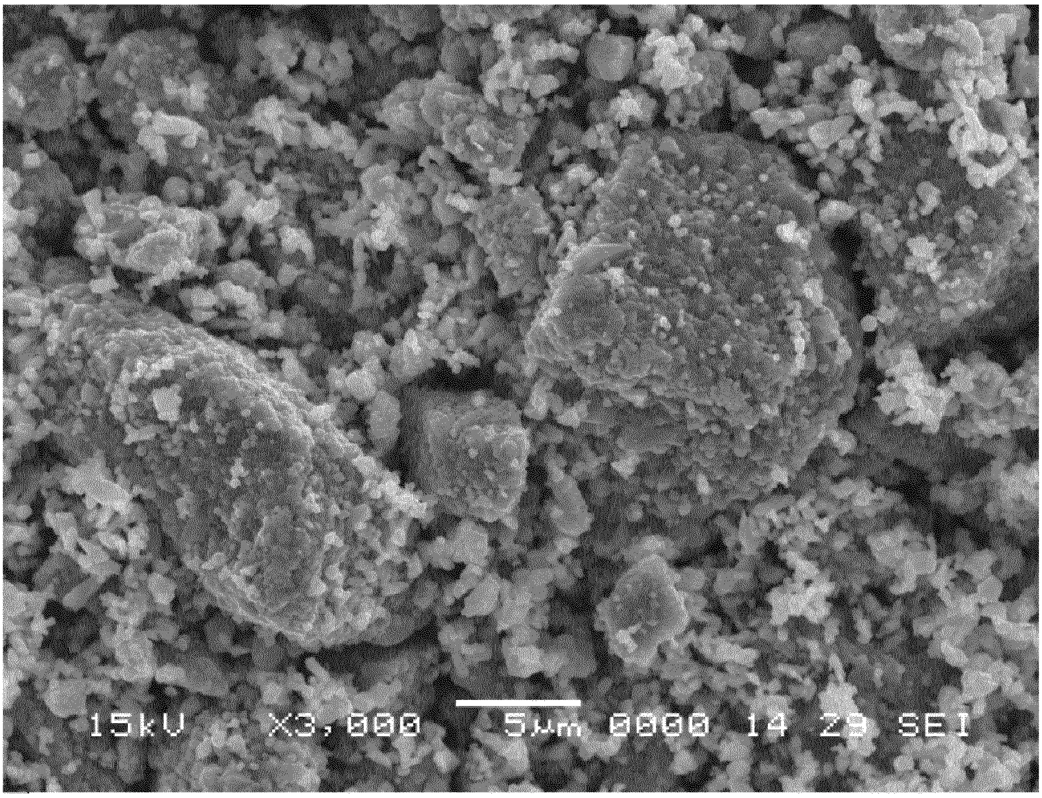
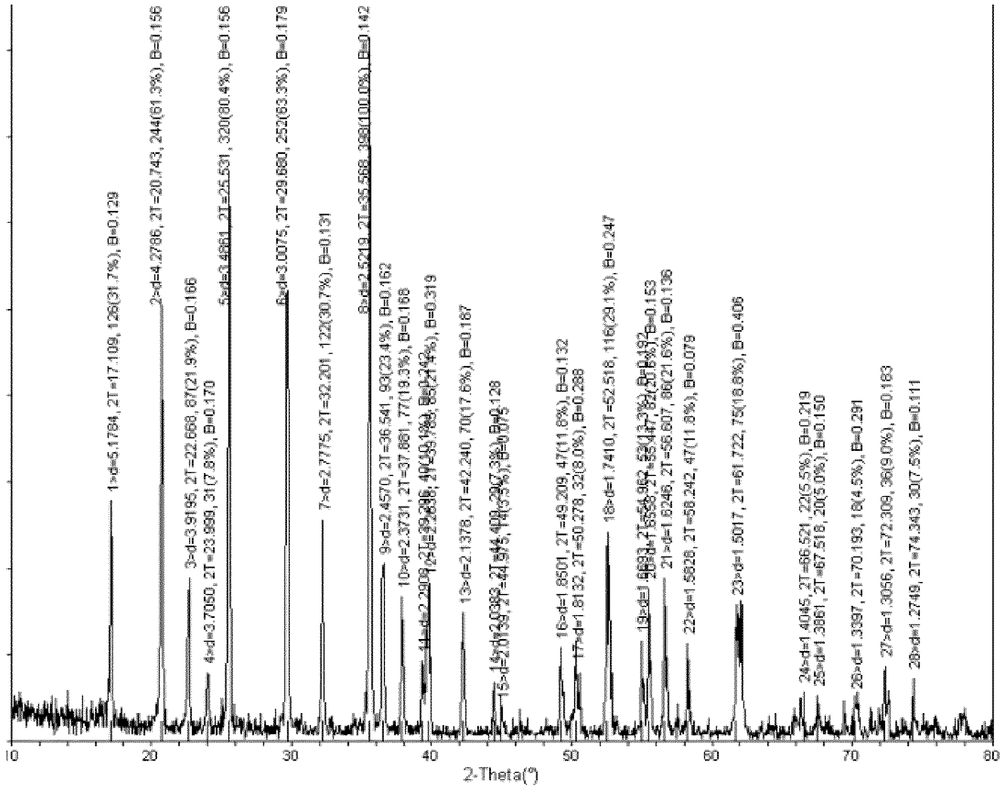

15kV
X3,000
5µm
0000
14 29
SEI

FIG.18


1>d=5.1784, 2T=17.109, 126(31.7%), B=0.129
2>d=4.2786, 2T=20.743, 244(61.3%), B=0.156
3>d=3.9195, 2T=22.668, 87(21.9%), B=0.166
4>d=3.7050, 2T=23.999, 31(7.8%), B=0.170
5>d=3.4861, 2T=25.531, 320(80.4%), B=0.156
6>d=3.0075, 2T=29.680, 252(63.3%), B=0.179
7>d=2.7775, 2T=32.201, 122(30.7%), B=0.131
8>d=2.5219, 2T=35.568, 398(100.0%), B=0.142
9>d=2.4570, 2T=36.541, 93(23.4%), B=0.162
10>d=2.3731, 2T=37.881, 77(19.3%), B=0.168
11>d=2.2909, 2T=39.296, 40(10.1%), B=0.242
12>d=2.2638, 2T=39.785, 85(21.4%), B=0.319
13>d=2.1378, 2T=42.240, 70(17.6%), B=0.187
14>d=2.0383, 2T=44.409, 29(7.3%), B=0.128
15>d=2.0139, 2T=44.975, 14(3.5%), B=0.075
16>d=1.8501, 2T=49.209, 47(11.8%), B=0.132
17>d=1.8132, 2T=50.278, 32(8.0%), B=0.288
18>d=1.7410, 2T=52.518, 116(29.1%), B=0.247
19>d=1.6693, 2T=54.962, 53(13.3%), B=0.192
20>d=1.6553, 2T=55.447, 82(20.6%), B=0.153
21>d=1.6246, 2T=56.607, 86(21.6%), B=0.136
22>d=1.5828, 2T=58.242, 47(11.8%), B=0.079
23>d=1.5017, 2T=61.722, 75(18.8%), B=0.406
24>d=1.4045, 2T=66.521, 22(5.5%), B=0.219
25>d=1.3861, 2T=67.518, 20(5.0%), B=0.150
26>d=1.3397, 2T=70.193, 18(4.5%), B=0.291
27>d=1.3056, 2T=72.309, 36(9.0%), B=0.183
28>d=1.2749, 2T=74.343, 30(7.5%), B=0.111
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2-Theta(°)

FIG.19

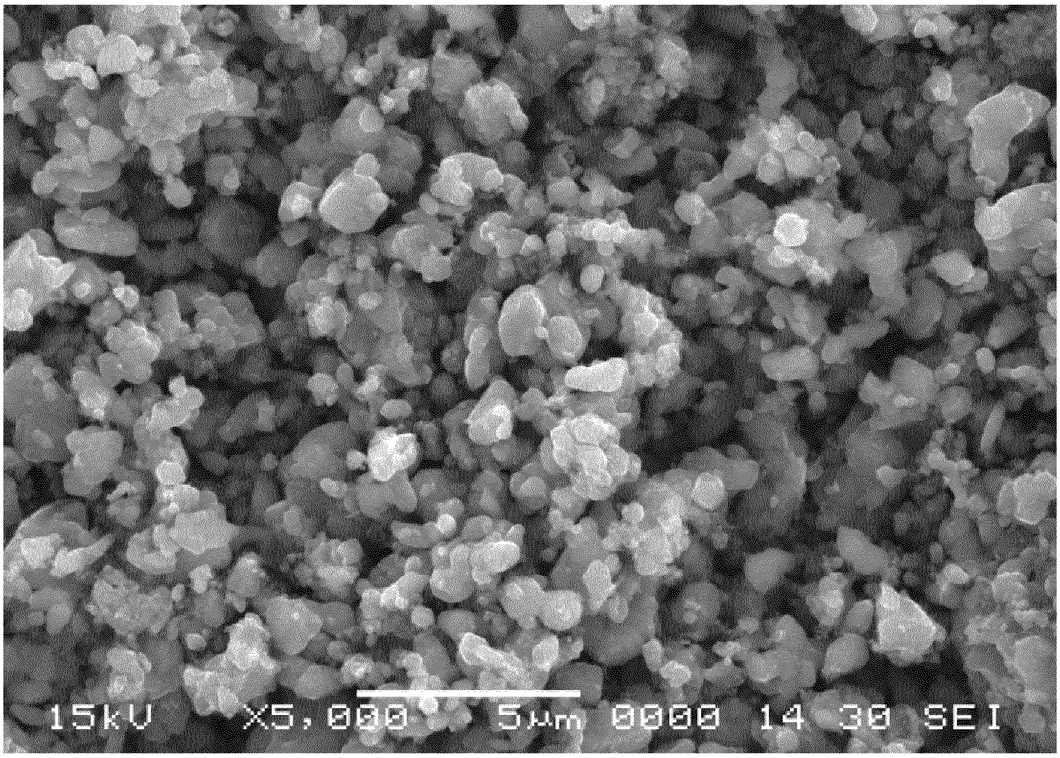
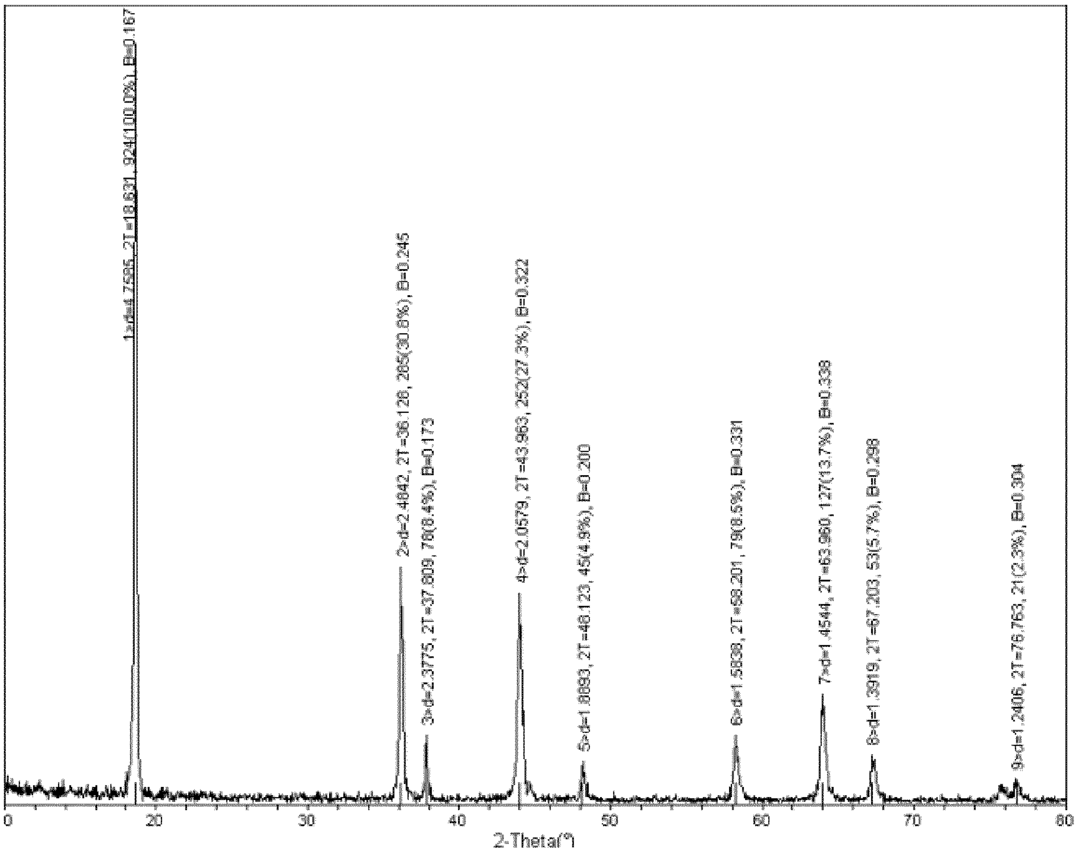

15kV X5,000 5μm 0000 14 30 SEI

FIG.20


1>d=4.7585, 2T=18.631, 924(100.0%), B=0.167
2>d=2.4842, 2T=36.128, 285(30.8%), B=0.245
3>d=2.3775, 2T=37.809, 78(8.4%), B=0.173
4>d=2.0579, 2T=43.963, 252(27.3%), B=0.322
5>d=1.8893, 2T=48.123, 45(4.9%), B=0.200
6>d=1.5838, 2T=58.201, 79(8.5%), B=0.331
7>d=1.4544, 2T=63.960, 127(13.7%), B=0.338
8>d=1.3919, 2T=67.203, 53(5.7%), B=0.298
9>d=1.2406, 2T=76.763, 21(2.3%), B=0.304
0
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50
60
70
80
2-Theta(°)

FIG.21

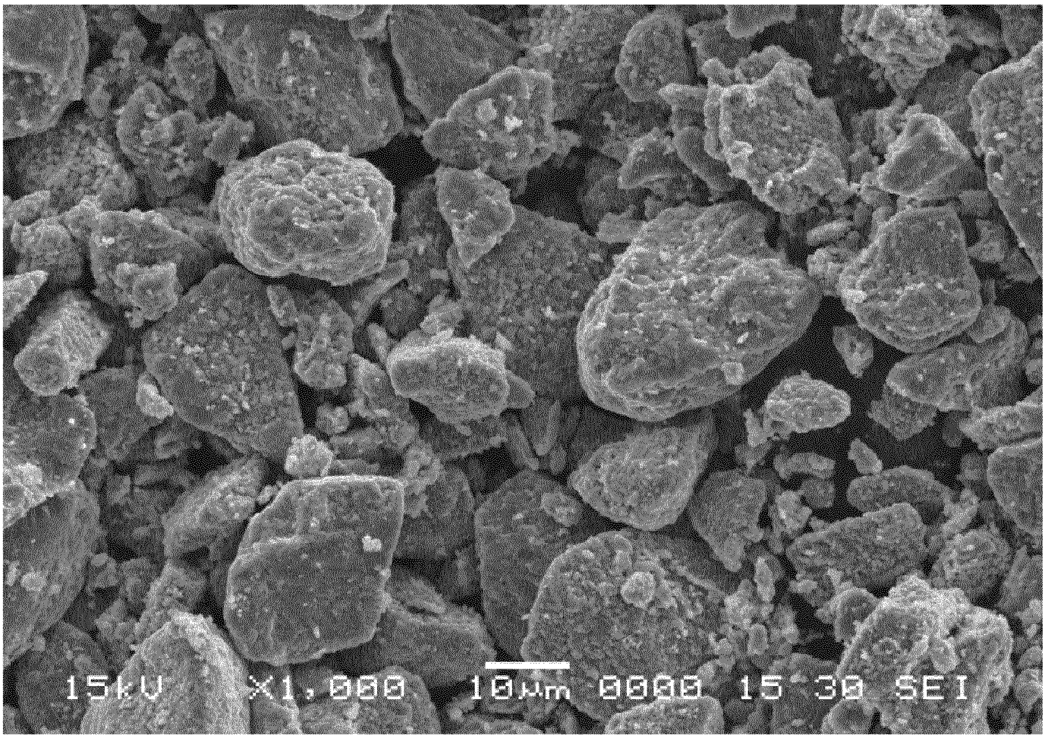
15kV X1,000 10μm 0000 15 30 SEI

FIG.22

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2009/076101

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01M4/-; H01M10/-; C01D15/-; C01G45/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC; WPI; CNKI; CNPAT: lithium, Li, polycrystal, Mn, manganese, anode, positive, crystal, battery, cell, cobalt, Co, nickel, Ni

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	CN101764222A(SHENZHEN ZHENHUA CHENE-CHEM CO.,LTD et al.) 30 Jun. 2010 (30.06.2010) claims 1-10	1-10
A	JP8-37007A(TOSOH CORP) 06 Feb. 1996 (06.02.1996) claims 1-4	1-10
A	CN1547277A(HUNAN JINGXIN TECHNOLOGY CO LTD) 17 Nov. 2004 (17.11.2004) claims 1-4 and example 1	1-10
A	CN1288871A(CHENGDU ORGANIC CHEM INST CAS) 28 Mar. 2001 (28.03.2001) the whole document	1-10

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search 16 Aug. 2010 (16.08.2010)	Date of mailing of the international search report **08 Oct. 2010 (08.10.2010)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer SHI Weiliang Telephone No. (86-10)62085010

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2009/076101

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN1838453A(UNIV CENT SOUTH) 27 Sep. 2006 (27.09.2006) the whole document	1-10
A	CN101510603A(JILIN JIEN NICKEL IND CO LTD) 19 Aug. 2009 (19.08.2009) the whole document	1-10
A	CN1847155A(CHINESE ACAD SCI SHANGHAI MICRO SYST INS) 18 Oct. 2006 (18.10.2006) the whole document	1-10

Form PCT/ISA /210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2009/076101

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN101764222A	2010-06-30	None	
JP8-37007A	1996-02-06	JP3550783B2	2004-08-04
CN1547277A	2004-11-17	CN1279639C	2006-10-11
CN1288871A	2001-03-28	CN1171826C	2004-10-20
CN1838453A	2006-09-27	CN100362681C	2008-01-16
CN101510603A	2009-08-19	None	
CN1847155A	2006-10-18	CN100372774C	2008-03-05

Form PCT/ISA /210 (patent family annex) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2009/076101

Continuation of:

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC:

H01M4/48(2010.01) i
H01M4/1391(2010.01) i
H01M10/0525(2010.01) i
C01D15/00(2006.01) n
C01G45/00(2006.01) n